

WASTE GLASS - A SUPPLEMENTARY CEMENTITIOUS MATERIAL

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Abstract

This study investigates the feasibility of using waste glass as a supplementary cementitious material, or SCM. By further defining some of the parameters by which waste glass may be incorporated into concrete as a cement replacement, the environmental, economical, and engineering benefits associated with the utilization of this waste stream as a value added product may be realized. There are several factors from past lines of research which have limited the acceptance of waste glass as a common SCM, including the production of alkali silica reaction (ASR) gel, and the lack of pozzolanic reactivity.

The current work details a mechanical treatment to improve reactivity and provides a particle size and percent addition at which waste glass performs comparably to ground granulated blast furnace slag (GGBFS) and nearly as well as silica fume (SF). Through continuous wet grinding in alcohol for up to 45 hours, it was possible to reduce the glass to a mean particle size of 6.6 μm . Although this was still larger than SF, the pozzolanic reactivity of the waste glass was clearly demonstrated through consumption of $\text{Ca}(\text{OH})_2$ and measured heat of hydration. Waste glass at a larger particle size (16.5 μm) was as reactive as GGBFS at the same particle size distribution. Use of waste glass at 10% replacement of Portland cement by mass and at a particle size below 100 μm proved useful as a SCM. Ground waste glass displayed surface characteristics similar to GGBFS as a result of the mechanical treatment.

A relationship between pozzolanic and alkali silica reaction (ASR) was identified in the laboratory results, where intermediate phases of the reaction were present in addition to the two extreme compositions. Calcium silicate hydrate (C-S-H) is the main reaction product of the pozzolanic reaction, with a Ca/Si ratio of 1.5-2. ASR products generally have a Ca/Si ratio of 0.01-1. The products observed with agglomeration of waste glass particles had a Ca/Si ratio which ranged from 0.5-2, and generally had higher alkali content than would be expected in C-S-H. The affects of silica concentration rather than particle size

and the role of the alkalinity of the solution on the reaction products were explored.

A distinct reaction rim was identified around glass agglomerates where fluorescence was observed. There was a higher than average alkali content in the reaction rim and gel around the agglomerate, and a lower than average silica content in the reaction rim and surrounding paste. The results indicate that ASR can be induced even in low alkalinity cement, and that the rate of reaction influences both the characteristics and composition of the reaction product. The reaction is influenced by pH and particle size, but another unidentified factor ultimately influences the product. ASR was initiated at sites with a high concentration of glass powder but did not follow the classic pessimum pattern of increased reactivity associated with intermediate particle sizes.

Publication List

This thesis consists of the following papers:

Paper I

Federico L. M. & Chidiac S. E. (2009). Waste glass as a supplementary cementitious material in concrete – Critical review of treatment methods. *Cement & Concrete Composites*, 31(8), 606-610.

Paper II

Federico L. M. & Chidiac S. E. (2013). Effects of particle size, grinding, and cement alkalinity on the reactivity of waste glass as a supplementary cementitious material. *Cement and Concrete Research*, submitted, reference # CEMCON-D-13-00408.

Paper III

Federico L. M., Chidiac S. E., & Raki L. (2011). Reactivity of cement mixtures containing waste glass using thermal analysis, *Journal of Thermal Analysis and Calorimetry*, 104(3), 849-858.

Permissions have been granted to reproduce the papers as part of this thesis by Elsevier for Paper I and Springer for Paper III.

Co-Authorship

This thesis has been prepared in accordance with the regulations provided by McMaster University Faculty of Graduate Studies for a sandwich thesis. The papers that make up this thesis have been co-authored, and the contribution of the co-authors is described for each publication.

Chapter 2 Waste glass as a supplementary cementitious material in concrete – Critical review of treatment methods, L. M. Federico & S. E. Chidiac

The extensive literature review was conducted by L. M. Federico. Data analysis was performed by L. M. Federico. The paper was developed and written by L. M. Federico, and edited by Dr. S. E. Chidiac.

Chapter 3 Effects of particle size, grinding, and cement alkalinity on the reactivity of waste glass as a supplementary cementitious material, L. M. Federico & S. E. Chidiac

The experimental testing program was conceived and developed by L. M. Federico in consultation with Dr. S. E. Chidiac. The testing was carried out by L. M. Federico. The analysis of the data was conducted by L. M. Federico under the supervision of Dr. S. E. Chidiac. The paper was conceived and written by L. M. Federico and edited by Dr. S. E. Chidiac.

Chapter 4 Reactivity of cement mixtures containing waste glass using thermal analysis, L. M. Federico, S. E. Chidiac, & L. Raki

The experimental testing program was conceived and developed by L. M. Federico in consultation with Dr. S. E. Chidiac and Dr. L. Raki. The testing was carried out by L. M. Federico under the supervision of Dr. S. E. Chidiac and Dr. L. Raki. The analysis of the data was conducted by L. M. Federico under the supervision of Dr. S. E. Chidiac. The paper was conceived and written by L. M. Federico and edited by Dr. S. E. Chidiac and Dr. L. Raki.

Declaration of Academic Achievement

The most significant contribution of this work to the field of Civil Engineering is the identification that alkali silica reactivity can be induced through agglomeration of finely ground glass at 10% replacement by mass in both high and low alkali cement. Previous observations have limited this effect to only silica fume in high alkali cement (Pettersson, 1992; Diamond, 1998; Maas, Ideker, & Juenger, 2007). There was a reverse pessimum effect observed for agglomeration size when compared to the same phenomenon for particle size in the literature. Theoretical predictions regarding the composition of the reaction rim with respect to alkalis and observed for other reactive materials (Wang & Gillott, 1991; Rivard, Ollivier, & Ballivy, 2002) were experimentally confirmed for agglomerated glass. There are also contributions made to the body of work characterizing ASR gel and supporting the use of ground waste glass as a supplementary cementitious material at particle sizes below 100 μm .

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To my husband Blair and all my family and friends, thank you for the endless supply of support, encouragement, interest, and confidence in my abilities. To my daughter Maëlle, thank you for the inspiration.

To my parents, I would like to express my love and extreme gratitude for everything, but especially for that which was most felt; your unconditional love, support and pride This thesis is dedicated to you both.

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Chapter 1 Thesis Summary

1.0 Introduction

The intent of this chapter is to provide a summary of the research which led to the publication of the papers that form this thesis. The background of the research field and pertinent information to form a general understanding of the material are provided, including a brief overview of the history of glass in concrete and the pozzolanic and alkali silica reactions. The motivation for research in this line of work is also presented, including the scope of work and the environmental implications on the concrete industry. A summary of the main contributions of each paper is provided, and suggestions are provided for a future work path.

1.1 Motivation for Research

The use of supplementary cementitious materials (SCMs) to offset a portion of the cement powder in concrete is a promising method for reducing the environmental impact of the industry. The most influential environmental concerns in the use of concrete for construction are the production of green house gases during the manufacturing of cement powder, and the consumption of non-renewable resources as raw materials. If an alternative material can be substituted for at least a portion of the cement powder that does not contribute additional green house gasses to the atmosphere, conserves natural resources, and does not negatively affect the properties of the resulting concrete, then the environmental impact of the industry can be reduced (Rehan & Nehdi, 2005; Aitcin, 2000). As an added incentive, researchers and manufacturers of cement and concrete have explored ways to not only offset the use of cement powder, but to improve the properties of the resulting concrete, reduce the cost of the materials, and further reduce environmental damage by utilizing streams of waste material as SCMs (Sobolev & Arikan, 2002). Materials containing calcium, aluminates, and amorphous phases of silica, in addition to other phases, can react within the environment of hydrating cement to provide a product which

shares some of the properties of Portland cement through a secondary reaction known as the pozzolanic reaction.

Several industrial by-products have been used successfully as SCMs, including silica fume (SF), ground granulated blast furnace slag (GGBFS), and fly ash. These materials are used to create blends of cement which can improve concrete durability, early and long term strength, workability, and economy (Hooton, 1986; Detwiler, Bhatti, & Bhattacharja, 1996). One material which has potential as a SCM but which has not yet achieved the same commercial success is waste bottle glass. Glass has a chemical composition and phase which is comparable to traditional SCMs. It is abundant, can be of low economic value and is often land filled, despite the increasing development of municipal recycling programs (Meyer, 2001; Byars, Meyer, & Zhu, 2003).

One of the contributing factors for the lack of pursuit of waste glass as a SCM is the possibility of a deleterious reaction between the alkalis in the cement pore solution and the silica of the glass, called alkali silica reaction (ASR) (Johnston, 1974; Kozlova, Millrath, Meyer, & Shimanovich, 2004; Shayan & Xu, 2004; Jin, 1998). When this reaction occurs in place of the pozzolanic reaction, the effects on the concrete can be devastating. Although there have been great strides towards understanding both the ASR and pozzolanic reactions, there are merely guidelines available which aim to reduce the likelihood of ASR reaction as measured through expansion by limiting the size of the waste glass and the alkalinity of the cement powder.

1.2 Scope and Objectives

The scope of this research aims to identify the difference between the ASR versus the pozzolanic reaction when waste glass is utilized as a SCM by first confirming the reactivity of waste glass as a pozzolan, comparing the reactivity of the waste glass to other more commonly used SCMs, and then identifying the role of factors such as cement pore solution alkalinity and particle

size of the glass on the resulting products. Detailed tracking of the reactions leading to both reaction products was attempted with state of the art equipment and procedures, and the characteristics and composition of the raw materials, mixtures, and reaction products were measured. This study included only clear bottle glass and two variables, alkalinity of the cement and particle size of the glass. The scope was also limited to experimental investigation.

Three main objectives of the research include:

- 1) Review the merits of using powdered waste glass as a supplementary cementitious material, replacing a portion of the cement powder used in concrete in order to improve the environmental impact of the concrete industry by reducing the green house gases produced and raw materials consumed in cement production, and by diverting a waste material from landfills.
- 2) Evaluate the reactivity of powdered waste glass as a supplementary cementitious material as compared to traditional materials, specifically silica fume and ground granulated blast furnace slag.
- 3) Explore the causes of alkali silica reactivity versus pozzolanic reactivity with powdered waste glass as a SCM, including cement alkalinity and particle size distribution.

1.3 Background

1.3.1 Cement Hydration

Cement powder consists of a combination of compounds, the most abundant of which are calcium silicates, calcium aluminates, and calcium aluminoferrites. The compounds form when the raw materials, generally limestone, clay, and shale, are combined and heated in a rotary kiln at 1300-1500°C. This heating releases CO₂ and H₂O during the cement compound formation. Upon combination with water, the compounds form hydrated phases,

including calcium silicate hydrate (C-S-H), and excess calcium hydroxide ($\text{Ca}(\text{OH})_2$). The C-S-H is the main binding phase and is therefore responsible for the characteristic strength of hardened concrete. (Kosmatka, Kerkhoff, Panarese, MacLeod, & McGrath, 2002)

The hydration of cement powder with water and aggregates to form concrete is described in part by many models, whereas the formation of C-S-H specifically is described in a model by Taylor (1986). Taylor introduces C-S-H phases (C-S-H(I) and C-S-H(II)) that are imperfect crystalline structures similar to tobermorite and jennite, respectively, with layered three-dimensional spacing depending on the level of hydration and relative humidity of the hydrate. In the model, the silicate chains are stacked with layers of $\text{Ca}(\text{OH})_2$, and substitutional ions such as Al^{3+} . The spacing is occupied by pore solution, which is most significantly a solution of alkali and hydroxyl ions.

The two components of the C-S-H, tobermorite and jennite, will occur in varying proportions depending on the path of the reaction, and will consist of different lengths of polymerization and amounts of interstitial $\text{Ca}(\text{OH})_2$. As a result, the composition of C-S-H is stoichiometrically variable, with the value of Ca/Si ranging from 1 to 1.9 (Chen, Thomas, Taylor, & Jennings, 2004; Taylor, 1997; Glasser F. P., 1992).

The pore solution of hydrating cement changes over time as the cement components dissolve into the water and the hydrated solid products leave the solution. The pore solution stabilizes within approximately 7 days to relatively consistent concentrations of hydroxyl and alkali ions, with only minor amounts of other components, so long as no other process is occurring. (Diamond, 1983; van Eijk & Brouwers, 2000; Lothenbach & Wieland, 2006; Goni, Lorenzo, Guerrero, & Hernandez, 1996; Diamond, 1989).

1.3.2 Supplementary Cementitious Materials

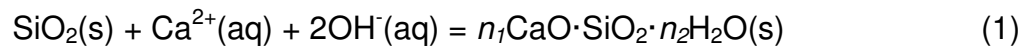
Supplementary cementitious materials are those which react in the pore solution of hydrating cement either hydraulically or pozzolanically, to create a product which contributes to the properties of hardened concrete. These can include natural pozzolans (clays, zeolites, diatomite) (Urhan, 1987), hydraulic materials other than Portland cement, and manufactured materials that can participate in a pozzolanic reaction (Cheriat, Cavalcante Rocha, & Pera, 1999; Escalante-Garcia, Gorokhovskiy, Mendoza, & Fuentes, 2003; Filipponi, Polettoni, Pomi, & Sirini, 2003; Pacewska, Bukowska, Wilinska, & Swat, 2002; Paya, Monzo, & Borrachero, 1999; Su, Fang, Chen, & Lui, 2000). Traditionally, the most widely used SCMs derived from a waste source are fly ash, GGBFS, and SF. In 2001, 11% of fly ash, 90% of GGBFS, and 185% of SF produced in Canada were used in the concrete industry as SCMs. In the case of SF and GGBFS, they were imported from other countries in order to meet the construction demand in Canada (Bouzoubaa & Fournier, 2005).

By replacing a percentage of the cement powder used in concrete with one of these materials, at least three benefits are realized; engineering, economic, and ecological. Engineering benefits include the optimization of certain properties of the fresh or hardened concrete, such as increasing strength through the use of SF. Economic benefits include, for example, the relatively lower cost of fly ash when compared to cement powder. Ecological benefits consider the decrease in CO₂ released and raw materials consumed as a result of less cement manufactured, and the use of materials otherwise bound for landfill (Malhotra & Mehta, 1996).

1.3.3 Pozzolanic Reactivity

The pozzolanic reaction occurs when amorphous silica dissolves into a solution with a high pH in the presence of calcium. In the pore solution of hydrating cement, there is an excess of Ca(OH)₂ in solution in a highly alkaline

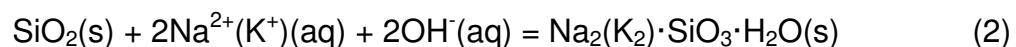
environment. If a material provides a readily soluble form of silica and a high surface area, the pozzolanic reaction will take place. The dissolved silica and the Ca(OH)_2 , along with substitutional alkalis and aluminates, will form a reaction product that can be chemically and structurally similar to C-S-H, according to the following equilibrium (Greenberg, 1961; Urhan, 1987):



As with C-S-H, the product composition is variable (n_1 and n_2), with a range in value of Ca/Si from 0.75 to 1.75 (Massazza, 1998).

1.3.4 Alkali Silica Reactivity

The alkali silica reaction and pozzolanic reaction share the same initial materials and have reaction products with similar chemical compositions but very different physical characteristics. While the pozzolanic reaction provides high calcium, low alkali material with properties similar to C-S-H, the ASR gel has high alkalis, low calcium, and does not contribute to strength, durability, or stability of the concrete. ASR gel can imbibe water and expand to create a pressure which, over time, can have detrimental effects on the concrete matrix (Diamond & Thaulow, 1974; Struble & Diamond, 1981). The equilibrium equation which drives the ASR is (Glasser & Kataoka, 1981):



When compared to Eq. 1, the similarity between the two is evident. Calcium is not presented in the equation, but is believed to be taken up by the gel through ion exchange with the potassium and sodium, and is thought to be necessary to initiate the detrimental swelling behavior characteristic to ASR (Scrivener & Monteiro, 1994; Dent Glasser & Kataoka, 1982; Chatterji, 1989;

Struble & Diamond, 1989; Wang & Gillott, 1991). The two reactions are closely related, as mixtures of the two components with differing proportions are often observed. The Ca/Si ratio of ASR gel can range from 0 to 0.5 (Helmuth & Stark, 1992; Wang & Gillott, 1992; Swamy, 1992) Figure 1.1 provides a general comparison of the composition of glass, ASR, C-S-H, and unhydrated cement powder.

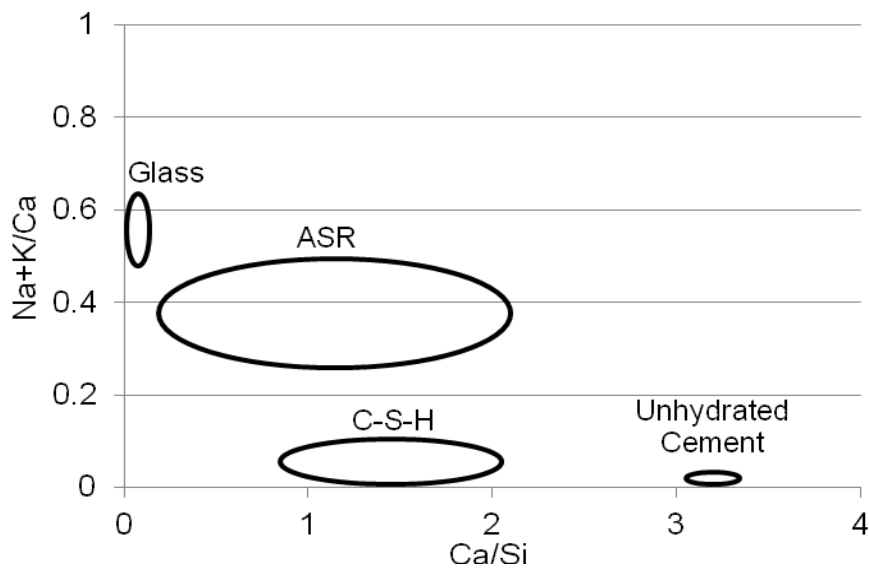


Figure 1.1 General composition of the materials observed in the current work.

Several methods have been developed to mitigate ASR in concrete in the presence of reactive materials. These methods include limiting the alkalinity of the concrete, including SCMs as a partial replacement for the cement, limiting the particle size of the reactive material, and using chemical treatments to prevent ASR formation. By limiting the alkalinity of the cement powder, the pore solution alkalinity is also limited. In this way, the dissolution of silica from the reactive material is less likely to occur in any significant amount, and any ASR gel formation will also be limited (Chatterji & Thaulow, 2000). By using a percentage of SCMs as a replacement for cement powder, a similar mechanism is employed. The SCMs reduce the alkalinity and as a result, slow the dissolution of silica.

Slower dissolution of silica favors the pozzolanic reaction. This reaction can further decrease the alkalinity of the pore solution by consuming $\text{Ca}(\text{OH})_2$ and incorporating alkali ions in to the pozzolanic C-S-H (Perry & Gillott, 1985; Chatterji, 1989; Monteiro, Wang, Sposito, dos Santos, & de Andrade, 1997; Bhatt, 1985). A relationship was established early in the research between the particle size of the reactive material and the resulting formation of ASR gel. Known as the pessimum effect, reactivity and resulting expansion is often maximized at an intermediate particle size. This effect is seen in Figure 1.2, which shows a sample of data from the literature where reactive aggregate is most expansive at an intermediate particle size.

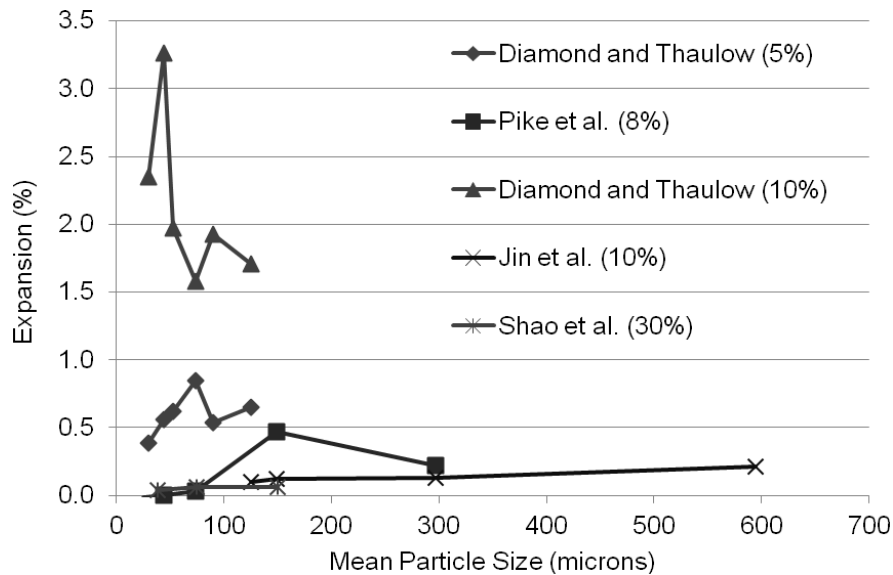


Figure 1.2 Mortar bar expansion versus glass particle size for various percent replacements (Federico & Chidiac, 2009)

Although the particle size at which expansion is minimized depends on the reactivity of the specific material, for most materials a particle range can be established to limit the production of ASR gel (Pike, Hubbard, & Insley, 1955; Diamond & Thaulow, 1974). A common chemical treatment to limit ASR is the

introduction of a lithium compound. The lithium slows the dissolution of silica, and prevents the repolymerization of the silica to form ASR gel. These treatments can affect the hydration products and introduce safety concerns (Diamond, 1999; Kurtis, Monteiro, & Meyer-Ilse, 2000; Kurtis & Monteiro, 2003; McCoy & Caldwell, 1951; Thomas, Hooper, & Stokes, 2000).

1.3.5 Waste Glass in Concrete

Waste glass can be used in concrete in three forms; as a large aggregate, as a small aggregate, and as a mineral additive (SCM). Generally when used as a large aggregate, waste glass can negatively affect strength, and can result in ASR (Johnston, 1974; Phillips, Cahn, & Keller, 1972). The use of glass as a large aggregate is also limited by the dimensional restrictions. Although the use of glass as a fine aggregate is more promising than that of a large aggregate (Topcu & Canbaz, 2004; Polley, Cramer, & de la Cruz, 1998; Panchakarla & Hall, 1996), it was identified that the most reliable way to limit ASR when using waste glass is to reduce the particle size below that of a fine aggregate (Meyer, Baxter, & Jin, 1996; Taha & Nounu, 2008; Carles-Gibergues, Cyr, Moisson, & Ringot, 2008; Kojima, Takagi, & Haruta, 2000). Following from this observation, the detailed study of the reduction of particle size determined that a particle size exists for each reactivity of glass composition at which ASR expansion is maximized, known as the pessimum effect; see Figure 1.2 (Jin, Meyer, & Baxter, 2000; Jin, 1998; Shayan & Xu, 2004).

1.3.6 Waste Glass as a SCM

The trends observed from the use of waste glass in concrete naturally progressed towards smaller particle sizes of glass, and ultimately to the use of waste glass as a SCM rather than an aggregate. There is not a clear particle size at which glass becomes pozzolanic, but there is little evidence of pozzolanic reactivity above 100 μm (Shao, Lefort, Moras, & Rodriguez, 2000; Dyer & Dhir,

2001; Chen, Huang, Wu, & Yang, 2006; Pereira de Oliveira, Castro Gomes, & Santos, 2007). The pozzolanic reactivity of fine waste glass is identified by an increase in C-S-H and decrease in Ca(OH)_2 (Sobolev, Turker, Soboleva, & Iscioglu, 2007).

Use of glass powder in the presence of reactive aggregates can actually mitigate ASR. Improved workability and durability were reported for concrete containing glass as a SCM. The compressive strength of concrete containing glass powder is lower than OPC at early ages, but continues to develop, approaching the control strength over time at addition up to 30%, and can surpass that of OPC in some cases. (Shayan & Xu, 2004; Meyer, Egosi, & Andela, 2001; Carles-Gibergues, Cyr, Moisson, & Ringot, 2008).

Comparisons of waste glass as a SCM when compared to fly ash indicate that waste glass at a similar particle size performs better than fly ash with respect to strength development at all ages. Expansion testing gave mixed results (Shao, Lefort, Moras, & Rodriguez, 2000; Chen, Huang, Wu, & Yang, 2006; Schwarz & Neithalath, 2008).

1.4 Summary of Papers

Paper I: Waste glass as a supplementary cementitious material in concrete – Critical review of treatment methods

As a result of the continued interest in reducing the environmental impact and improving the sustainability of the construction industry, waste glass was chosen as an underutilized SCM resource. A review of the literature was undertaken to identify the challenges facing the use of waste glass as a SCM, and to assess the treatment methods that may be employed in order to improve its appeal. Alkali silica reaction was identified as the greatest challenge to the acceptance of waste glass as a common SCM since it is not possible to predict the reaction product with any refined level of control. The benefits of utilizing waste glass as a SCM include a reduction in the CO_2 emission and non-

renewable resource consumption associated with the production of Portland cement powder, and the diversion and value addition to a material that is otherwise sent to landfill. Based on a review of the literature, at a particle size below 300 μm , pozzolanic reactivity is most likely to occur; however, a range of values makes it apparent that additional research is required. A replacement of 10% Portland cement with waste glass as a SCM does not result in any major loss of strength in the resulting concrete. Possible treatments are explored to improve pozzolanic reactivity, where chemical treatment offers the best results. The results of the literature review were used to formulate a laboratory testing program to further understand the usefulness of waste glass as a SCM.

Paper II: Effects of particle size and grinding on the reactivity of waste glass as a supplementary cementitious material in low and high alkali cement

Mechanical treatment in the form of grinding was used to reduce the particle size distribution of clear bottle glass to represent a similar particle size distribution to GGBFS and SF in order to determine the usefulness of waste glass as a SCM when compared to these typical SCMs. Laser particle size analysis and the BET gas sorption method were used to determine particle size distribution and surface area, respectively. Portland cement with low and high alkalinity (0.44 and 0.72 Na_2O equivalent, respectively) was replaced with 10% waste glass by mass at a constant water to cementing materials ratio. In order to determine the pozzolanic reactivity of the mixtures, calorimetry was used to measure the heat of hydration, and X-ray diffraction to identify the phases of the raw materials and reaction products. It was confirmed that a decrease in particle size can improve reactivity, and that at the same particle size distribution, waste glass is as reactive as GGBFS in both high and low alkali cement. It was not possible to recreate the reactivity of SF. Certain phases, including syngenite, were identified in the reaction product, and may influence the reaction by temporarily impacting the pH.

Paper III: Reactivity of cement mixtures containing waste glass using thermal analysis

The results of a laboratory study to investigate the potential of waste glass as a SCM led to the generation of ASR gel in mixtures containing agglomerates of small glass particles. The reactivity of the glass was compared to two other typical SCMs; SF and GGBFS. Thermal analysis was used to measure the type and degree of the reaction products. Electron microscopy was used to measure the chemical composition and microstructural characteristics of the reaction products. Ultraviolet optical microscopy was used to identify ASR gel. At a mean particle size of 16.5 μm and 6.6 μm , waste glass is pozzolanic based on $\text{Ca}(\text{OH})_2$ consumption and does not induce ASR. Even at very small agglomerate sizes ($< 0.5 \mu\text{m}^2$), ASR was induced. A relationship analogous to the pessimum effect for particles was observed for the production of ASR at agglomerate sites, where intermediate sized agglomerates ($0.1\text{-}0.31 \mu\text{m}^2$) are less likely to present an ASR composition. This observation presents as a reverse of the pessimum effect observed for particles. The high concentration of the glass particles, rather than the size of the individual glass particles, was sufficient to induce ASR, and low alkalinity of the cement was not sufficient to prevent the ASR formation. Contrary to what might be expected from past observations, less ASR occurred in the high alkali cement mixtures. In this work, the theory that ASR and C-S-H are essentially two extremes of the same reaction, with a range of intermediate compositions, is demonstrated. The reaction rim plays a significant role in the ultimate composition of the reaction product.

1.5 Conclusions

In relation to the main objectives outlined in Section 1.2, the following conclusions can be drawn from the research performed towards the topic of waste glass as a SCM.

The literature review presented in the first paper provided the following conclusions:

- 1) Waste glass, when compared to fly ash, is a useful SCM. Based on its chemical composition, it has the potential to perform as well as SF and GGBFS through some form of activation, such as mechanical or chemical.
- 2) There is a lack of data in the literature to compare waste glass to SF and GGBFS as a SCM.
- 3) The use of waste glass as a SCM is currently inhibited by the historical observations of ASR between glass and cement.
- 4) Using waste glass as a SCM can further improve the sustainability of the concrete industry.

The laboratory research described in the second paper, as well as analysis of the observations led to the following conclusions:

- 5) Clean, clear bottle glass can be used as a supplementary cementitious material at cement replacement levels of up to 10% by mass in both high and low alkali cement at particle sizes below 100 μm .
- 6) Well dispersed glass powder supports pozzolanic reaction, adding to the C-S-H matrix of the hydrated cement, and does not produce ASR gel.
- 7) By offsetting the use of 10% of the cement powder, the CO_2 release associated with cement production and the consumption of non-renewable resources can be decreased accordingly.
- 8) Ground bottle glass can be equally as reactive as GGBFS when utilized at a comparable particle size. Grinding the glass is a practical treatment method to improve its reactivity to that of GGBFS.
- 9) When compared to SF, waste glass is not as reactive when mechanically treated through grinding to improve reactivity, since the same particle size distribution could not be achieved.

In the third paper, further analysis to understand the observations in the laboratory provided the following conclusions:

- 10) At two particle size distributions (mean particle size 16.5 and 6.6 μm) and in a high alkali and low alkali cement at 10% cement replacement, ASR was not observed through ultraviolet optical microscopy.
- 11) When very fine glass (mean particle size of 6.6 μm) agglomerated together, ASR could be, but was not necessarily, initiated at these locations.
- 12) At the site of ASR, the reaction product could range in composition from low calcium C-S-H to high alkali, low calcium gel, and several intermediate compositions. This confirms the postulation that ASR and C-S-H are extreme products of the same reaction.
- 13) Zones of distinct compositions (including reaction rims) were identified but were not directly related to agglomerate size or cement alkalinity.
- 14) The observation of ASR product was less likely at intermediate sizes of glass agglomerate, presenting a reverse of the pessimum effect of particles, where the greatest reactivity occurred at the small and large agglomerates.
- 15) ASR was observed in both high and low alkali cement; however, the composition of the reaction products was different in each cement. It is therefore not possible to generally state that low alkali cement will prevent ASR, while high alkali cement will induce it.

1.6 Suggestions for Future Work

- A simplified system consisting of amorphous silica and a synthetic pore solution to represent both high and low alkali cements should be developed in order to track in more detail the composition of the reactants and products. The pH of the mixtures should be continuously tracked or sampled at short time intervals in

order to determine if the pH of the solution is altered and how it affects the concentration of each alkali ion.

-The solubility of amorphous silica at a known and consistent spherical particle size should be determined in the synthetic pore solution in order to determine the influence of other cement components on the silica solubility.

- The laboratory values determined for solubility, ion concentration, pH and reactant and product composition should be used to develop a model which will predict the composition of the product for the simplified system.

- An experimental program should be designed in which the packing density of very fine glass powder into a range of sizes of agglomerates is controlled and then exposed to synthetic pore solution to induce ASR. The reactants, products, and pH should be measured. The unique products and reaction rims observed for the high density amorphous silica could help define the details of the relationship between ASR and C-S-H, and determine how each factor (silica concentration, agglomerate size, and solution alkalinity) influence the observed products. This research would be extensive, but would help explain some of the unexpected observations associated with ASR induced at agglomerates rather than particles.

- Waste glass from a municipal stream should be obtained and the experiments repeated to compare its performance to common SCMs in order to define the impact of any impurities or glass composition variation on the observed results.

- Waste glass at a mean particle size of 16.5 μm should be used at 10% replacement in a high alkali and low alkali concrete mixture in order to define the impact on concrete strength and durability of waste glass as a SCM.

1.7 References

- Aitcin, P.-C. (2000). Cements of yesterday and today - concrete of tomorrow. *Cement and Concrete Research*, 30, 1349-1359.
- Bhatty, M. S. (1985). Mechanism of pozzolanic reactions and control of alkali-aggregate expansion. *Cement, Concrete, and Aggregates, CCAGDP*, 7(2), 69-77.
- Bouzoubaa, N., & Fournier, B. (2005). Current situation with the production and use of supplementary cementitious materials (SCMs) in concrete construction in Canada. *Canadian Journal of Civil Engineering*, 32(1), 129-143.
- Byars, E., Meyer, C., & Zhu, H. Y. (2003). Use of waste glass for construction products: legislative and technical issues. In R. K. Dhir, M. D. Newlands, & J. E. Halliday (Ed.), *Recycling and Reuse of Waste Materials* (pp. 827-838). London: Thomas Telford Ltd.
- Carles-Gibergues, A., Cyr, M., Moisson, M., & Ringot, E. (2008). A simple way to mitigate alkali-silica reaction. *Materials and Structures*, 41, 73-83.
- Chatterji, S. (1989). Mechanisms of alkali-silica reaction and expansion. In K. Okada, S. Nishibayashi, & M. Kawamura (Ed.), *8th International Conference on Alkali-Aggregate Reaction* (pp. 101-105). New York: Elsevier.
- Chatterji, S., & Thaulow, N. (2000). Some fundamental aspects of alkali-silica reaction. In M. A. Berube, B. Fournier, & B. Durand (Ed.), *Alkali-Aggregate Reaction in Concrete* (pp. 21-29). Quebec: Universite Laval.

- Chen, C. H., Huang, R., Wu, J. K., & Yang, C. C. (2006). Waste e-glass particles used in cementitious mixtures. *Cement and Concrete Research*, *36*(3), 449-456.
- Chen, J. J., Thomas, J. J., Taylor, H. F., & Jennings, H. M. (2004). Solubility and structure of calcium silicate hydrate. *Cement and Concrete Research*, *34*, 1499-1519.
- Cherif, M., Cavalcante Rocha, J., & Pera, J. (1999). Pozzolanic properties of pulverized coal combustion bottom ash. *Cement and Concrete Research*, *29*, 1387-1391.
- Dent Glasser, L. S., & Kataoka, N. (1982). On the role of calcium in the alkali-aggregate reaction. *Cement and Concrete Research*, *12*, 321-331.
- Detwiler, R. J., Bhatt, J. I., & Bhattacharja, S. (1996). *Supplementary Cementing Materials for Use in Blended Cements*. Skokie, Illinois, U.S.A.: Research and Development Bulletin RD112T, Portland Cement Association.
- Diamond, S. (1983). Effects of microsilica (silica fume) on pore-solution chemistry of cement pastes. *Journal of Thermal Analysis and Calorimetry*, *104*(3), 82-84.
- Diamond, S. (1989). ASR- Another look at mechanisms. In K. Okada, S. Nishibayashi, & M. Kawamura (Ed.), *8th International Conference on Alkali-Aggregate Reaction* (pp. 83-94). New York: Elsevier.
- Diamond, S. (1998). Silica fume agglomerates and alkali silica reaction. In J.-P. Bournazel, & Y. Malier (Ed.), *International Conference on Concrete: from Material to Structure* (pp. 98-106). RILEM.

- Diamond, S. (1999). Unique response of LiNO_3 as an alkali silica reaction-preventative admixture. *Cement and Concrete Research*, 29(8), 1271-1275.
- Diamond, S., & Thaulow, N. (1974). A study of expansion due to alkali-silica reaction as conditioned by the grain size of the reactive aggregate. *Cement and Concrete Research*, 4, 591-607.
- Dyer, T. D., & Dhir, R. K. (2001). Chemical reactions of glass cullet used as cement component. *Journal of Materials in Civil Engineering*, 13(6), 412-417.
- Escalante-Garcia, J. I., Gorokhovskiy, A. V., Mendoza, G., & Fuentes, A. F. (2003). Effect of geothermal waste on strength and microstructure of alkali-activated slag cement mortars. *Cement and Concrete Research*, 33, 1567-1574.
- Federico, L. M. & Chidiac, S. E. (2009). Waste glass as a supplementary cementitious material in concrete – critical review of treatment methods. *Cement & Concrete Composites*, 31, 606-610.
- Filipponi, P., Poletini, A., Pomi, R., & Sirini, P. (2003). Physical and mechanical properties of cement-based products containing incineration bottom ash. *Waste Management*, 23, 145-156.
- Glasser, F. P. (1992). Chemistry of the alkali-aggregate reaction. In R. N. Swamy, *The Alkali-Silica Reaction in Concrete* (pp. 31-53). Glasgow: Blackie and Son Ltd.
- Glasser, L. S., & Kataoka, N. (1981). The chemistry of `alkali-aggregate` reaction. *Cement and Concrete Research*, 11(1), 1-9.

- Goni, S., Lorenzo, M. P., Guerrero, A., & Hernandez, M. S. (1996). Calcium hydroxide saturation factors in the pore solution of hydrated Portland cement fly ash pastes. *Journal of the American Ceramic Society*, 79(4), 1041-1046.
- Greenberg, S. A. (1961). Reaction between silica and calcium hydroxide solutions. I. Kinetics in the temperature range 30 to 85. *Journal of Physical Chemistry*, 65(12), 12-16.
- Helmuth, R., & Stark, D. (1992). Alkali-silica reactivity mechanisms. In J. Skalny (Ed.), *Materials Science of Concrete III* (pp. 131-208). Ohio: The American Ceramic Society.
- Hooton, R. D. (1986). Permeability and pore structure of cement pastes containing fly ash, slag, and silica fume. In G. Frohnsdorff (Ed.), *Blended Cements, ASTM STP 897* (pp. 128-143). Philadelphia: American Society for Testing and Materials.
- Jin, W. (1998). *Alkali-silica reaction in concrete with glass aggregate-A chemophysico-mechanical approach, PhD Thesis*. New York: Columbia University.
- Jin, W., Meyer, C., & Baxter, S. (2000). "Glascrete"- concrete with glass aggregate. *ACI Materials Journal*, 97(2), 208-213.
- Johnston, C. D. (1974). Waste glass as a coarse aggregate for concrete. *Journal of Testing and Evaluation*, 2(5), 344-350.
- Kojima, T., Takagi, N., & Haruta, K. (2000). Expanding characteristics of mortar with glass powder produced from waste bottles. In M. A. Berube, B. Fournier, & B. Durand (Ed.), *Alkali-Aggregate Reaction in Concrete* (pp. 673-682). Quebec City: Universite Laval.

- Kosmatka, S. H., Kerkhoff, B., Panarese, W. C., MacLeod, N. F., & McGrath, R. J. (2002). *Design and Control of Concrete Mixtures, EB 101, 7th edition*. Ottawa: Cement Association of Canada.
- Kozlova, S., Millrath, K., Meyer, C., & Shimanovich, S. (2004). A suggested screening test for ASR in cement-bound composites containing glass aggregate based on autoclaving. *Cement & Concrete Composites, 26*, 827-835.
- Kurtis, K. E., & Monteiro, P. J. (2003). Chemical additives to control expansion of alkali-silica reaction gel: proposed mechanisms of control. *Journal of Materials Science, 38*, 2027-2036.
- Kurtis, K. E., Monteiro, P. J., & Meyer-Ilse, W. (2000). Examination of the effects of lithium chloride on ASR gel expansion. In M. A. Berube, B. Fournier, & B. Durand (Ed.), *Alkali-Aggregate Reaction in Concrete* (pp. 51-60). Quebec: Universite Laval.
- Lothenbach, B., & Wieland, E. (2006). A thermodynamic approach to the hydration of sulphate-resisting Portland cement. *Waste Management, 26*, 706-719.
- Maas, A. J., Ideker, J. H., & Juenger, M. C. (2007). Alkali silica reactivity of agglomerated silica fume. *Cement and Concrete Research, 37*, 166-174.
- Malhotra, V. M., & Mehta, P. K. (1996). Pozzolanic and Cementitious Materials. In V. M. Malhotra, *Advances In Concrete Technology* (Vol. 1). Amsterdam: Gordon and Breach Publishers.
- Massazza, F. (1998). Pozzolana and pozzolanic cements. In P. C. Hewlett (Ed.), *Lea's Chemistry of Cement and Concrete* (4th Edition ed., pp. 471-636). Oxford: Elsevier.

- McCoy, W. J., & Caldwell, A. G. (1951). New approach to inhibiting alkali-aggregate expansion. *Journal of the American Concrete Institute*, 22(9), 693-706.
- Meyer, C. (2001). Recycled glass - from waste material to valuable resource. In R. K. Dhir, M. C. Limbachiya, & T. D. Dyer (Ed.), *Recycling and Reuse of Glass Cullet* (pp. 1-10). London: Thomas Telford Ltd.
- Meyer, C., Baxter, S., & Jin, W. (1996). Potential of waste glass for concrete masonry blocks. In K. P. Chong (Ed.), *Materials for a New Millenium: Proceedings of the Fourth Materials Engineering Conference* (pp. 666-673). Washington, D.C.: ASCE.
- Meyer, C., Egosi, N., & Andela, C. (2001). Concrete with waste glass as aggregate. *Proceedings of the International Symposium Concrete Technology Unit of ASCE and University of Dundee*, (p. 179). Dundee.
- Monteiro, P. J., Wang, K., Sposito, G., dos Santos, M. C., & de Andrade, W. P. (1997). Influence of mineral admixtures on the alkali-aggregate reaction. *Cement and Concrete Research*, 27(12), 1899-1909.
- Pacewska, B., Bukowska, M., Wilinska, I., & Swat, M. (2002). Modification of the properties of concrete by a new pozzolan: A waste catalyst from the catalytic process in a fluidized bed. *Cement and Concrete Research*, 32(11), 145-152.
- Panchakarla, V. S., & Hall, M. W. (1996). Glascrete?-disposing of non-recyclable glass. In K. Chong (Ed.), *Materials for the New Millennium* (pp. 509-518). New York: American Society of Civil Engineers.

- Paya, J., Monzo, J., & Borrachero, M. V. (1999). Fluid catalytic cracking catalys residue (FC3R) An excellent mineral by-product for improving early-strength developement of cement mixtures. *Cement and Concrete Research*, 29, 1773-1779.
- Pereira de Oliveira, L. A., Castro Gomes, J. P., & Santos, P. (2007). Optimization of pozzolanic reaction of ground waste glass incorporated in cement mortars. In L. Braganca, M. Pinheiro, S. Jalali, R. Mateus, R. Amoeda, & M. Correia Guedes (Ed.), *SB07 Sustainable Construction, Materials and Practices: Challenge of the Industry for the New Millennium* (pp. 928-934). Lisbon: IOS Press.
- Perry, C., & Gillott, J. E. (1985). The feasibility of using silica fume to control concrete expansion due to alkali-aggregate reaction. *Durability of Building Materials*, 3, 133-146.
- Pettersson, K. (1992). Effects of silica fume on alkali-silica expansion in mortar specimens. *Cement and Concrete Research*, 22(1), 15-22.
- Phillips, J. C., Cahn, D. S., & Keller, G. W. (1972). Refuse glass aggregate in portland cement concrete. In M. A. Schwartz (Ed.), *Proceeding of the Third Mineral Waste Utilization Symposium* (pp. 385-390). Chicago: IIT Research Institute.
- Pike, R. G., Hubbard, D., & Insley, H. (1955). Mechanisms of alkali-aggregate reaction. *ACI Journal Proceedings*, 52, 13-34.
- Polley, C., Cramer, S., & de la Cruz, R. V. (1998). Potential for using waste glass in Portland cement concrete. *Journal of Materials in Civil Engineering*, 10(4), 210-219.

- Rehan, R., & Nehdi, M. (2005). Carbon dioxide emissions and climate change: policy implications for the cement industry. *Environmental Science & Policy*, 8, 105-114.
- Rivard, P., Ollivier, J.-P., & Ballivy, G. (2002). Characterization of the ASR rim application to the Potsdam sandstone. *Cement and Concrete Research*, 32, 1259-1267.
- Schwarz, N., & Neithalath, N. (2008). Influence of a fine glass powder on cement hydration: Comparison to fly ash and modeling the degree of hydration. *Cement & Concrete Composites*, 30, 486-496.
- Scrivener, K. L., & Monteiro, P. J. (1994). The alkali-silica reaction in a monolithic opal. *Journal of the American Ceramic Society*, 77(11), 2849-2856.
- Shao, Y., Lefort, T., Moras, S., & Rodriguez, D. (2000). Studies on concrete containing ground waste glass. *Cement and Concrete Research*, 30(1), 91-100.
- Shayan, A., & Xu, A. (2004). Value-added utilization of waste glass in concrete. *Cement and Concrete Research*, 34(1), 81-89.
- Sobolev, K., & Arikan, M. (2002). High volume mineral additive for eco-cement. *American Ceramic Society Bulletin*, 81(1), 39-43.
- Sobolev, K., Turker, P., Soboleva, S., & Iscioglu, G. (2007). Utilization of waste glass in ECO-cement: Strength properties and microstructural observations. *Waste Management*, 27, 971-976.
- Struble, L. J., & Diamond, S. (1981). Swelling properties of synthetic alkali silica gels. *Journal of the American Ceramic Society*, 64(11), 652-655.

- Struble, L., & Diamond, S. (1989). Influence of cement pore solution on expansion. In K. Okada, S. Nishibayashi, & M. Kawamura (Ed.), *8th International Conference on Alkali-Aggregate Reaction* (pp. 167-172). New York: Elsevier.
- Su, N., Fang, H.-Y., Chen, Z.-H., & Lui, F.-S. (2000). Reuse of waste catalyst from petrochemical industries for cement substitution. *Cement and Concrete Research*, *30*, 1773-1783.
- Swamy, R. N. (1992). *The Alkali-Silica Reaction in Concrete*. Glasgow: Blackie and Son Ltd.
- Taha, B., & Nounu, G. (2008). Properties of concrete contains mixed colour waste recycled glass as sand and cement replacement. *Construction and Building Materials*, *22*(5), 713-720.
- Taylor, H. F. (1986). Proposed structure for calcium silicate hydrate gel. *Journal of the American Ceramic Society*, *69*(6), 464-467.
- Taylor, H. F. (1997). *Cement Chemistry* (2nd Edition ed.). London: Thomas Telford.
- Thomas, M. D., Hooper, R., & Stokes, D. (2000). Use of lithium-containing compounds to control expansion in concrete due to alkali-silica reaction. In M. A. Berube, B. Fournier, & B. Durand (Ed.), *Alkali-Aggregate Reaction in Concrete* (pp. 783-792). Quebec: Universit e Laval.
- Topcu, I. B., & Canbaz, M. (2004). Properties of concrete containing waste glass. *Cement and Concrete Research*, *34*(2), 267-274.
- Urhan, S. (1987). Alkali silica and pozzolanic reactions in concrete. Part 1: Interpretation of published results and an hypothesis concerning the mechanism. *Cement and Concrete Research*, *17*(1), 141-152.

- van Eijk, R. J., & Brouwers, H. J. (2000). Prediction of hydroxyl concentrations in cement pore water using a numerical cement hydration model. *Cement and Concrete Research*, 30, 1801-1806.
- Wang, H., & Gillott, J. E. (1991). Mechanism of alkali-silica reaction and the significance of calcium hydroxide. *Cement and Concrete Research*, 21, 647-654.
- Wang, H., & Gillott, J. E. (1992). Competitive nature of alkali-silica fume and alkali-aggregate (silica) reaction. *Magazine of Concrete Research*, 44(161), 235-239.

Chapter 2 Waste glass as a supplementary cementitious material in concrete – Critical review of treatment methods

Federico L. M. & Chidiac S. E. (2009). Waste glass as a supplementary cementitious material in concrete – Critical review of treatment methods. *Cement & Concrete Composites*, 31(8), 606-610.

Abstract

Concrete is the most widely used construction material and, for the most part, is produced using non-renewable natural resources and energy intensive processes which emit green house gasses. There exists an opportunity to improve the sustainability of this industry by further exploring the use of alternative materials. As an aggregate, glass bottle waste has faced specific challenges including bond, ASR gel production, and strength degradation of the concrete. This paper reviews the literature pertaining to incorporate waste glass into concrete as a supplementary cementing material. Pozzolanic properties of waste glass as an SCM and ASR are related to particle size and percent addition. Lithium additives control ASR expansion; however, the mechanism of this control has yet to be defined.

Keywords: SCM; waste glass; pozzolan; ASR; sustainability; lithium

2.0 Introduction

The concept of utilizing waste material for building applications has a long and successful history, which includes fly ash, slag, and silica fume. These once problematic, land filled waste materials are now considered valuable commodities for use in enhancing certain properties of concrete. A waste material which continues to face challenges as a component of concrete is bottle glass. The

benefits of developing alternative or supplementary cementing materials as partial replacements for ordinary Portland cement (OPC) powder are described by Malhotra and Mehta [1], who divide them into ecological, economic, and engineering categories.

Ecological or environmental benefits of alternative materials include (1) the diversion of non-recycled waste from landfills for useful applications, (2) the reduction in the negative effects of producing cement powder, namely the consumption of non-renewable natural resources, (3) the reduction in the use of energy for cement production and (4) the corresponding emission of greenhouse gasses. The economic benefits of using alternative materials are best realized in situations where the cost of the alternative material is less than that of cement powder while providing comparable performance. This cost must consider the source of the alternative material, its transportation, processing, and should consider savings through diversion, such as tipping fees and landfill management costs. The engineering or technical benefits of alternative materials are realized when a specialized use for such material may be developed, such that the use of the alternative material is more desirable than use of concrete made with OPC alone.

There exists an opportunity to realize these potential benefits even in communities where recycling programs are in place. Although a curb side recycling program has meant increasing rates of recycling in Ontario since 1987, only 68% of alcohol containers, for example, are recovered through recycling programs, and much of this material is broken and of mixed colour, making high value recycling difficult and impractical. As a result, waste glass can often end up in landfills [2]. Alcohol containers alone make up 44% of curb side recycled material, and by 2015, these containers are predicted to contribute 116,000 tonnes of material to the collection stream [3].

Early attempts to incorporate waste glass in concrete tended to focus on aggregate replacement. The properties of glass seemed comparable to those of

large aggregate in terms of constitution, strength and durability, and the larger size of the glass meant lower processing costs. These early attempts however, were unsuccessful due to the alkali-silica reaction (ASR) which takes place in the presence of the amorphous waste glass and concrete pore solution. In addition to ASR, several other challenges exist in incorporating waste glass into concrete. Using waste bottle glass limits the size and shape of particles for coarse aggregate. The maximum size of one dimension of the aggregate will always be the thickness of the bottle. Crushed waste bottles will therefore tend to form large aggregate which is flat and elongated, and may negatively affect workability [4], and which has been attributed to observed decreases in compressive strength [5]. Waste glass also presents a challenge in terms of contamination and consistency in the waste stream. Most waste glass that cannot be recycled is broken and of mixed colour, which will cause variation in the chemical composition of the waste. There may be contamination due to paper and plastic labels, caps and corks, and sugars remaining from the original use and content of the bottles [6]. Moreover, seasonal fluctuation in the waste stream would be expected.

In order to overcome the limitations of ASR, several treatment methods were explored, which generally included mechanical and chemical treatments. In exploring these methods, key developments have been made. Experimentation using mechanical treatments looked at reducing the particle size of the waste glass through grinding. The results of this work indicated that as the particle size of the waste glass was decreased, the tendency for ASR formation also decreased. Furthermore, the results yielded an increase in the compressive strength of concrete made with very fine waste glass [7,8]. Chemical treatments were initially explored in detail by McCoy and Caldwell [9], where a series of salts, acids, organic and proprietary compounds, and proteins were used in mortar bars containing Pyrex glass in an effort to identify which materials may

reduce ASR. This series of tests indicated that the use of lithium compounds significantly reduced ASR related expansion.

This paper provides a critical review of research initiatives reported in the literature whose aim is to improve the feasibility of incorporating waste glass into concrete through various treatments. The review is weighted on the progress made to develop waste glass into a viable Supplementary Cementing Material (SCM). The focus of waste glass utilization has shifted in more recent years from aggregate to mineral additive in light of the observations related to particle size.

2.1 Challenge of ASR in the Use of Waste Glass

Use of waste glass in concrete first focused on aggregate replacement. Phillips and Cahn [6] attempted to introduce waste glass as a partial replacement of the fine and coarse aggregate in concrete masonry block, the production and use of which is less conducive to ASR gel production, and which allow early age monitoring. Using amber glass in a high-alkali, fine cement, tested properties of the blocks generally fell near or within accepted limits, although strength gain was slow and below typical at 28 days. Phillips and Cahn observed that the main challenges in utilizing waste glass would be the removal of contamination, processing, and cost. Johnston [4] also considered waste glass as a coarse aggregate, and found that only by using low alkali cement or high percentages of pozzolans such as fly ash could satisfactory strength and expansion performance be achieved to one year.

The obvious challenges encountered during this preliminary work deterred interest in the idea of alternative uses for waste glass in the concrete industry for many years. In the last decade of the 20th century, a resurgence in interest has developed as a result of increased awareness of several social and global elements, including green house gas emissions and energy costs.

Experimentation with the addition of waste glass in concrete has been closely related to the study of alkali-silica reactivity, where production of ASR gel in the presence of reactive aggregates causes damaging expansion in concrete. The topic of ASR reactivity has been thoroughly covered in the past 30 years. In this discussion, it is important to impart only that the mechanism by which a reactive aggregate can form ASR gel, leading to expansion and ultimately causing damage to concrete, is dependent on the presence of amorphous silica, which is the major component of waste glass, the presence of alkali hydroxides in pore solution, and cement reaction products [10]. An early study by Diamond and Thaulow aimed to determine the relationship between ASR production and reactive particle size, revealed that there is no limiting size for reaction. However, they observed that the reaction rate is greater at finer particle sizes [11]. Work by Shayan and Xu [7], as well as Jin [8], indicated that a decrease in particle size leads to a pessimum effect in terms of ASR expansion which was related to an increase in reactivity. Jin et al. [12] further hypothesized that the pessimum observed is related to a competition between ASR rate of reaction and rate of transport of ASR gel away from the reaction site, where at a certain particle size, the reaction rate is great enough and the transport rate low enough that a maximum expansion is observed. Figure 2.1 shows some of these results, where depending on the glass composition and environment, a maximum ASR expansion tends to occur at an intermediate value. For most cases, both the local maximum and minimum expansion occurs at a very small particle size, typically less than 100 μm [11-14].

Effectiveness of methods such as chemical treatment and surface abrasion in improving the performance of concrete containing waste glass through prevention of expansive behaviour, and the effect of different glass colours on ASR expansion was reported by Meyer [15]. Polley et al. observed a pessimum effect with respect to the percentage of waste glass added to the concrete as a replacement of fine aggregate combined with fly ash [16]. A

pessimism percentage was also observed by Kawamura and Fuwa [17], but not by Jin et al. [12].

Both the degree of reaction and the nature of the products are known to influence the ASR damage associated with the use of waste glass. Many attempts have been made to predict the swelling behaviour of the gel based on either the chemical composition of the initial reactants or the reaction product itself. Although a relationship has been observed between the ratio of alkali and silica in the gel and the resulting swellability [18-20], the relationship is too complex to allow accurate prediction due to localized variation in chemical composition of the gel.

2.2 Waste Glass as a Pozzolan

One of the limiting factors in the use of alternative materials as pozzolans in concrete is the lower reactivity of the materials when compared to cement powder. Overcoming this limitation requires practical methods for increasing the reactivity of SCMs. Shi and Day [21] effectively used salts as chemical activators to increase the reactivity of natural pozzolans, as well as several other methods, including mechanical and thermal treatments [22]. A comparison of the methods by Shi and Day indicated that the most effective method for developing reactivity in natural pozzolans was chemical activation, which improved both the initial reaction rate and the final strength. The reactivity of the treated pozzolanic material was measured in terms of the compressive strength and total hydration of the material.

The chemical compositions of some of the pozzolans are compared to the composition of waste glass in Table 2.1. With the exception of Al_2O_3 and CaO , the percentages of the main constituents are similar [21,23-26]. It is reasonable to expect that some success may be achieved by applying similar treatment to waste glass in order to improve its pozzolanic properties. The properties which

influence the pozzolanic behaviour of waste glass, and most pozzolans in general, are fineness, composition, and the pore solution present for reaction. Based on observed compressive strengths, Meyer et al. [27] postulated that below 45 μm , glass may become pozzolanic. The pozzolanic properties of glass are first notable at particle sizes below approximately 300 μm , and below 100 μm , glass can have a pozzolanic reactivity which is greater than that of fly ash at low percent cement replacement levels and after 90 days of curing [26,28].

The pozzolanic reactivity of fine waste glass is observed as an increase in compressive strength, which can be seen in Figure 2.2. In the reported data [26, 14], compressive strength is highest for specimens containing very fine glass (<100 μm), and the strength decreases as particle size increases. Figure 2.3 [7,14,29-33] shows the effect of percentages of waste glass replacing OPC and fine aggregate on the compressive strength of mortar bars. The results show that a cement replacement between 10% and 20% yields the highest strength, while fine aggregate replacement of up to 40% has little effect on compressive strength.

2.3 Lithium Treatments

The use of lithium compounds has been explored for ASR mitigation as well as promoting pozzolanic reactivity. Some of the compounds which have been explored include lithium carbonate (Li_2CO_3) [34,17] lithium hydroxide (LiOH) [35,36], lithium nitrate (LiNO_3) [37,38], lithium chloride (LiCl) [39] and lithium fluoride (LiF) [40]. Lithium is unique among the alkali metals because it has the smallest atomic radius to possess the single valence electron in this group, yet a comparatively large hydrated radius and polarizing power. The properties of concrete and mortar specimens containing waste glass treated with lithium are also unique. Using lithium to stabilize dissolved silica, Lawrence and Vivian [36] were able to demonstrate that silica was slower to dissolve in the presence of

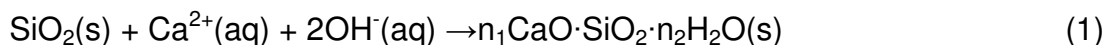
lithium, and the product had different properties than that of other alkalis. Confirmed using ^{29}Si -NMR by Wijnen et al. [41], this low dissolution rate was accompanied by a lack of repolymerization of the silica species and the presence of a microcrystalline lithium silicate precipitate (Li_2SiO_3). Both silica dissolution and lack of repolymerization, as well as aggregation of particles, were observed by Kurtis et al. [39,42] using imaging techniques. While several authors have observed a decrease in dissolved silica in the presence of various lithium compounds, using LiOH specifically can result in an increase in dissolved Si while still mitigating ASR expansion [37,43,44]. The lack of repolymerization and the formation of aggregated or crystallized products are hypothesized to be related to the lack of ASR expansion in the presence of lithium. Figure 2.4 shows expansion measured over an extended time frame as it relates to the Li/Na ratio of the product for various lithium treatments [35,45,46]. For most cases, there is a minimum expansion observed at an intermediate value of Li/Na, however; depending on the reactive aggregate used, expansion may still exceed acceptable limits [46].

Work by Ramyar [40] attempted to relate the Ca/Si ratio of products in the presence of lithium compounds to the resulting structure, where two distinct products, massive and crystalline, were observed. However, no clear relationship could be determined. A decrease in CaO/SiO_2 was related to larger expansion with the exception of LiF as an additive. Further observations of the product of ASR reactions containing lithium by Kawamura and Fuwa [17] show that the CaO/SiO_2 ratio decreases and becomes more consistent throughout the sample as the lithium content is increased, and the resulting expansion is decreased, most notably for dosages of lithium greater than 0.5%. This result has in turn been related to the ratio of lithium to total alkali, where a threshold ratio to control expansion has been identified as ranging between 0.6 and 0.9, depending on the experimental program and the material tested [47]. There is a narrow range for the ideal concentration of lithium in the system, which may indicate a pessimum

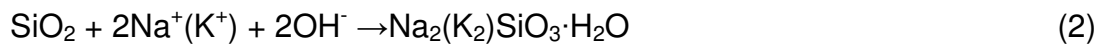
due to the additional OH^- liberated by the lithium compound [37,44,48]. Thomas et al. have observed that outside of the ideal lithium content, increased expansion may actually occur when compared to the control specimen [49]. Primary challenges still facing the use of lithium treatments include the absorption of large amounts of added lithium into the early hydration product, which, once absorbed, may not be available in later life, the increase in OH^- concentration [37], and the concerns of safety when working with reactive materials.

2.4 Waste Glass as an SCM

The use of any supplementary cementing material will depend on its performance, namely its strength, durability, and volumetric stability over time. In the case of waste glass, this performance is further challenged by the tendency for ASR to occur. The controlling process between a beneficial pozzolanic reaction, which would improve the performance of glass as an SCM, and a damaging ASR is the production of either a stable or swelling product. Depending on several factors, including calcium content, particle size, and alkalinity, the dissolved silica will repolymerize into expansive gel, hydrate into C-S-H, or a combination of both [48]. A theoretical mechanism by Urhan [50] suggests that at any time in a concrete containing either reactive aggregate or pozzolanic material, ASR gel and C-S-H, as well as a range of intermediate products, can be found. According to this mechanism, availability of calcium ions in combination with a relatively high rate of C-S-H formation will favour the pozzolanic reaction, and over time, any ASR product will take on the texture of C-S-H. When reacting as a pozzolan, glass powder will follow Eq. (1) [50], and the product will be a type of calcium silicate hydrate.



When the reaction of glass results in ASR gel, the chemical equation is similar, however, sodium, potassium, or other alkalis may be substituted for calcium as shown by Eq. (2) [18].



The final product is more likely similar to a precipitate of the composition given in Eq. (3), existing within a sol/gel matrix of calcium silicate hydrate with a $\text{Na}_2\text{O}/\text{SiO}_2$ ratio near 0.19.



This system may be the cause of variability in the swelling properties of ASR products [51].

Wang and Gillott [52], as well as Jin [8] have suggested that the mechanism which differentiates between pozzolanic and ASR products could be simply the degree of aggregation or particle size of the silica source. They postulated that the two reactions will compete with one another and the ease with which calcium ions can reach the pozzolanic reaction leads to a more stable and less expansive product. The question remains as to the specific role of lithium within the reaction product and its observed ability to control expansion in the system for various particle sizes and rates of reaction. In addition, the ability of LiOH to increase pozzolanic reactivity while decreasing ASR in the presence of glass or reactive aggregates seems contradictory.

The use of waste glass as a supplementary cementing material has demonstrated mixed results over a range of concentrations, particle sizes, and treatments, as was shown in Figure 2.2 and Figure 2.3. According to the requirements of ASTM standards [53] for the use of natural pozzolans, Table 2.2, glass has the potential to acceptably function as an SCM. However, proper

methods must be developed to control the ASR/pozzolanic reaction and influence a non-destructive, non-swelling product. The form of this product has not been identified. It may be a lithium silicate, or perhaps a pozzolanic form of C-S-H, which has the potential to contribute additional strength.

2.5 Concluding Remarks

The success or lack thereof in utilizing waste glass in concrete can be attributed to observed ASR damage. Although the collective understanding of ASR has improved dramatically through extensive research, it is still not possible to predict damage based on either the composition of the reactants or the reaction product. This prevents a fine level of control over the reaction.

As researchers moved from waste glass as an aggregate to waste glass as a replacement for OPC, pozzolanic properties were observed at particle sizes below 300 μm . These pozzolanic properties, however, are relatively weak, especially at larger particle sizes, and require enhancement. One possible form of enhancement used for natural pozzolans was chemical treatment.

The similarity between the ASR and pozzolanic reactions observed for waste glass in concrete suggests that they are closely related and may be simply various stages of one another subject to several controlling factors, including particle size, pore solution, and chemical composition.

Treatments with lithium appear to control the reaction by limiting the ASR expansion; however, the application of these treatments is not yet understood.

There is still a very clear gap in understanding the exact mechanism at work and the role of lithium compounds in the mechanism of control.

Acknowledgements

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References

- [1] V. M. Malhotra and P. K. Mehta. Pozzolanic and cementitious materials. In: *Advances in Concrete Technology*. New York: Gordon and Breach Publishers, 1996.
- [2] R. Siddique. *Waste materials and by-products in concrete*. New York: Springer Berlin Heidelberg, 2008.
- [3] Entec Consulting Ltd. *Report on Ontario blue box material recovery facilities*. 2007.
- [4] C. D. Johnston. Waste glass as coarse aggregate for concrete. *J Test Eval* 1974; 2(5): 344-350.
- [5] I. B. Topcu and M. Canbaz. Properties of concrete containing waste glass. *Cem Con Res* 2004; 34:267-274.
- [6] J. C. Phillips, D. S. Cahn, and G. W. Keller. Refuse glass aggregate in Portland cement concrete. In: *Proceeding of the Third Mineral Waste Utilization Symposium*. Chicago:1972. p. 163.
- [7] A. Shayan and A. Xu. Value-added utilization of waste glass in concrete. *Cem Con Res* 2004; 34(1):81-89.
- [8] W. Jin. *Alkali-silica reaction in concrete with glass aggregate-A chemophysico-mechanical approach*. PhD thesis. New York, Columbia University, 1998.

- [9] W. J. McCoy and A. G. Caldwell. New approach to inhibiting alkali-aggregate expansion. *J Amer Concrete Inst* 1951; 22(9):693-706.
- [10] S. Diamond. ASR-another look at mechanism. In: 8th International Conference on Alkali-Aggregate Reaction. Kyoto: Elsevier Applied Science, 1989. p. 83-94.
- [11] S. Diamond and N. Thaulow. A study of expansion due to alkali-silica reaction as conditioned by the grain size of the reactive aggregate. *Cem Conc Res* 1974;4(4):591-607.
- [12] W. Jin, C. Meyer, and S. Baxter. "Glasscrete"-concrete with glass aggregate. *ACI Materials Journal* 2000;97(2):208-213.
- [13] R. G. Pike, D. Hubbard, and H. Insley. Mechanisms of alkali-aggregate reaction. *ACI Journal Proceedings* 1955;52:13-34.
- [14] Y. Shao, T. Lefort, S. Moras, and D. Rodriguez. Studies on concrete containing ground waste glass. *Cem Con Res* 2000;30(1):91-100.
- [15] C. Meyer. Cracking an ASR barrier. *Concrete Producer* 2001.
- [16] C. Polley, S. M. Cramer, and R. V. de la Cruz. Potential for using waste glass in Portland cement concrete. *Journal of Materials in Civil Engineering* 1998;10(4):210-219.
- [17] M. Kawamura and H. Fuwa. Effects of lithium salts on ASR gel composition and expansion of mortars. *Cem Conc Res* 2003;33(6):913-919.
- [18] L. S. Dent Glasser and N. Kataoka. The chemistry of "alkali-aggregate" reaction. *Cem Conc Res* 1981;11:1-9.
- [19] W. C. Hansen. Studies relating to the mechanism by which the alkali-aggregate reaction produces expansion in concrete. *J Amer Concrete Inst*,1944; 15(3):213-227.
- [20] M.S. Tang, Z.Z. Xu, and S.F. Han. Alkali reactivity of glass aggregate. *Durability of Building Materials* 1987;4(4):377-385.
- [21] C. Shi and R. L. Day. Chemical activation of blended cements made with lime and natural pozzolans," *Cem Conc Res* 1993;23(6); 1389-1396.

- [22] C. Shi and R. L. Day. Comparison of different methods for enhancing reactivity of pozzolans. *Cem Conc Res* 2001;31:813-818.
- [23] S.E. Chidiac and L.M. Federico. Effects of waste glass additions on the properties and durability of fired clay brick. *Can J Civ Eng* 2007;34(11):1458-1466.
- [24] S. H. Kosmatka, B. Kerkhoff, W. C. Panarese, N. F. MacLeod, and R. J. McGrath. Design and control of concrete mixtures, EB 101. 7th Edition. Ottawa: Cement Association of Canada, 2002.
- [25] V. G. Papadakis, E. J. Pedersen, and H. Lindgreen. An AFM-SEM investigation of the effect of silica fume and fly ash on cement paste microstructure. *Journal of Materials Science* 1999;34:683-690.
- [26] C. Shi, Y. Wu, C. Riefler, and H. Wang. Characteristics and pozzolanic reactivity of glass powders. *Cem Conc Res* 2005;35(5):987-993.
- [27] C. Meyer, S. Baxter, and W. Jin. Potential of waste glass for concrete masonry blocks. In: *Proceedings of the Fourth Materials Engineering Conference*. Washington, 1996. p. 666-673.
- [28] N. Schwarz, H. Cam, and N. Neithalath. Influence of a fine glass powder on the durability characteristics of concrete and its comparison to fly ash. *Cem Conc Comp* 2008;30(6):486-496
- [29] C. Meyer, N. Egosi, and C. Andela. Concrete with waste glass as aggregate. In: *Proceedings of the International Symposium Concrete Technology Unit of ASCE and University of Dundee*. Dundee, 2001. p. 179.
- [30] S. Laldji and A. Tagnit-Hamou. Glass frit for concrete structures: a new, alternative cementitious material. *Canadian Journal of Civil Engineering* 2007;34(7):793-802.
- [31] V. S. Panchakarla and M. W. Hall. Glascrete?-disposing of non-recyclable glass. In: *Proceeding of ASCE 4th Materials Engineering Conference*. Washington, 1996. p. 509-518.

- [32] C. H. Chen, R. Huang, J. K. Wu, and C. C. Yang. Waste e-glass particles used in cementitious mixtures. *Cem Conc Res* 2006;36(3):449-456.
- [33] M. J. Terro. Properties of concrete made with recycled crushed glass at elevated temperatures. *Building and Environment* 2006;41:633-639.
- [34] I. B. Topcu, A. Raif Boga, and T. Bilir. Alkali-silica reactions of mortars produced by using waste glass as fine aggregate and admixtures such as fly ash and Li_2CO_3 . *Waste Management* 2007.
- [35] X. Mo, C. Yu, and Z. Xu. Long-term effectiveness and mechanism of LiOH in inhibiting alkali-silica reaction. *Cem Conc Res* 2003;33:115-119.
- [36] M. Lawrence and H. E. Vivian. The reaction of various alkalis with silica. *Aust J Appl Sci* 1961;12:96-103.
- [37] S. Diamond. Unique response of LiNO_3 as an alkali silica reaction-preventative admixture. *Cem Conc Res* 1999;29:1271-1275.
- [38] C. L. Collins, J. H. Ideker, G. S. Willis, and K. E. Kurtis. Examination of the effects of LiOH , LiCl , and LiNO_3 on alkali-silica reaction. *Cem Conc Res* 2004;34:1403-1415.
- [39] K. E. Kurtis and P. J. M. Monteiro. Chemical additives to control expansion of alkali-silica reaction gel: proposed mechanisms of control. *Journal of Material Science* 2003;38:2027-2036.
- [40] K. Ramyar, O. Copuroglu, O. Andic, and A. L. A. Fraaij. Comparison of alkali-silica reaction products of fly-ash- or lithium-salt-bearing mortar under long term accelerated curing. *Cem Conc Res* 2004;34:1179-1183.
- [41] P. W. J. G. Wijnen, et al. Silica gel dissolution in aqueous alkali metal hydroxides studied by ^{29}Si -NMR. *J Non-Crystalline Solids* 1989;109:85-94.
- [42] K. E. Kurtis, P. J. M. Monteiro, and W. Meyer-Ilse. Examination of the effects of LiCl on ASR gel expansion. In: 11th International Conference on Alkali-Aggregate Reaction. Quebec, 2000. p. 51-60.
- [43] Y. Qi and W. Zi-yun. Effects of lithium hydroxide on alkali silica reaction gels created with opal. *Construction and Building Materials* 2007;21:1656-1660.

- [44] X. Feng, M. D. A. Thomas, T. W. Bremner, B. J. Balcom, and K. J. Folliard. Studies on lithium salts to mitigate ASR-induced expansion in new concrete: a critical review. *Cem Conc Res* 2005;35:1789-1796.
- [45] J. S. Lumley. ASR Suppression by lithium compounds. *Cem Conc Res*, 1997;27(2):235-244.
- [46] B. Durand. More results about the use of lithium salts and mineral admixtures to inhibit ASR in concrete. In: 11th International Conference on Alkali-Aggregate Reaction. Quebec, 2000. p. 623-631.
- [47] Y. Sakaguchi, et al. The inhibiting effects of lithium compounds on alkali-silica reaction. In: 8th International Conference on Alkali-Aggregate Reaction. Kyoto, 1989. p. 229-234.
- [48] A. Buchwald, C. Kaps, and M. Hohmann. Alkali-activated binders and pozzolan cement binders-compete binder reaction or two sides of the same story? In: Proceedings of the 11th International Congress on the Chemistry of Cement (ICCC). Durban, 2003, pp. 1238-1246.
- [49] M. D. A. Thomas, R. Hooper, and D. Stokes. Use of lithium-containing compounds to control expansion in concrete due to alkali-silica reaction. In: 11th International Conference on Alkali-Aggregate Reaction. Quebec, 2000. p. 783-791.
- [50] S. Urhan. Alkali silica and pozzolanic reactions in concrete. Part 1: Interpretation of published results and an hypothesis concerning the mechanism. *Cem Conc Res* 1987;17(1): 141-152.
- [51] R. Helmuth, D. Stark, S. Diamond, and M. Monranville-Regourd. Alkali-silica reactivity, an overview of research, SHRP-C-342. Washington: National Research Council, 1993.
- [52] H. Wang and J. E. Gillott. Competitive nature of alkali-silica fume and alkali-aggregate (silica) reaction. *Mag Conc Res* 1992;44(161):235-239.

[53] ASTM International. C 618: Specification for coal fly ash and raw or calcined natural pozzolan for use in concrete. West Conshohocken: ASTM International, 2005.

Table 2.1 Chemical composition of waste glass and other pozzolans

Compound	Waste Glass [23]	Volcanic Ash [21]	Volcanic Pumice [21]	Slag [24]	Silica Fume [25]	High Ca Fly Ash [25]	OPC [25]
SiO ₂	63.79	73.68	65.74	35	90.9	39.21	20.33
Al ₂ O ₃	3.02	12.25	16.72	12	1.12	16.22	4.65
Fe ₂ O ₃	1.57	2.2	3.58	1	1.46	6.58	3.04
CaO	13.01	1.13	3.33	40	0.69	22.78	61.78
MgO	0.89	0.23	0.95	-	0.77	2.35	3.29
K ₂ O	0.54	3.95	3.05	-	-	-	0.59
Na ₂ O	11.72	3.6	4.48	.3	-	-	0.24
SO ₃	0.165	0.32	0.65	9	0.38	4.3	3.63
LOI	4.55	3.05	2.4	1	3	2.1	-

Table 2.2 Pozzolans from Table 1 as SCMs, qualification under ASTM standards

ASTM C 618-05 Requirements [52]		Waste Glass	Slag	Silica Fume	Fly Ash
SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃ , min %	70	68.38	48	93.48	62.04
SO ₃ , max %	4	0.165	9	0.38	4.3
Moisture Content, max %	3	-	-	-	-
LOI, max %	10	4.55	1	3	2.1

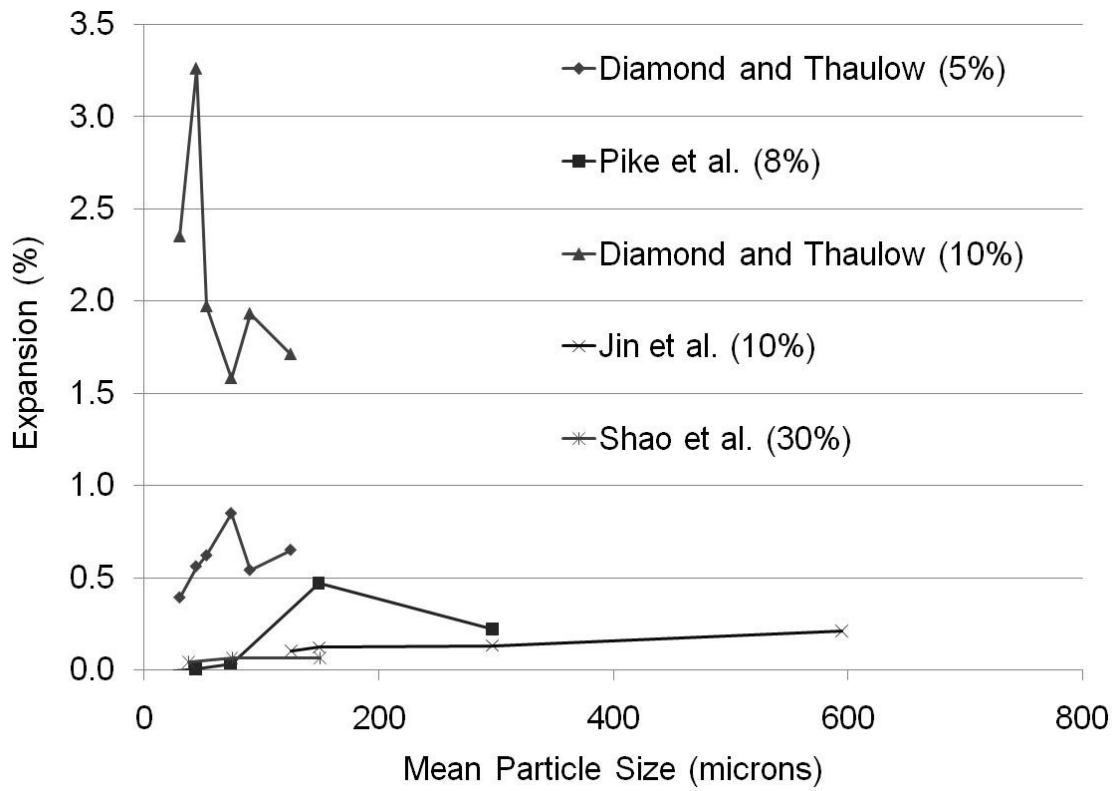


Figure 2.1 Expansion vs. glass particle size for various percent replacements [11-14]

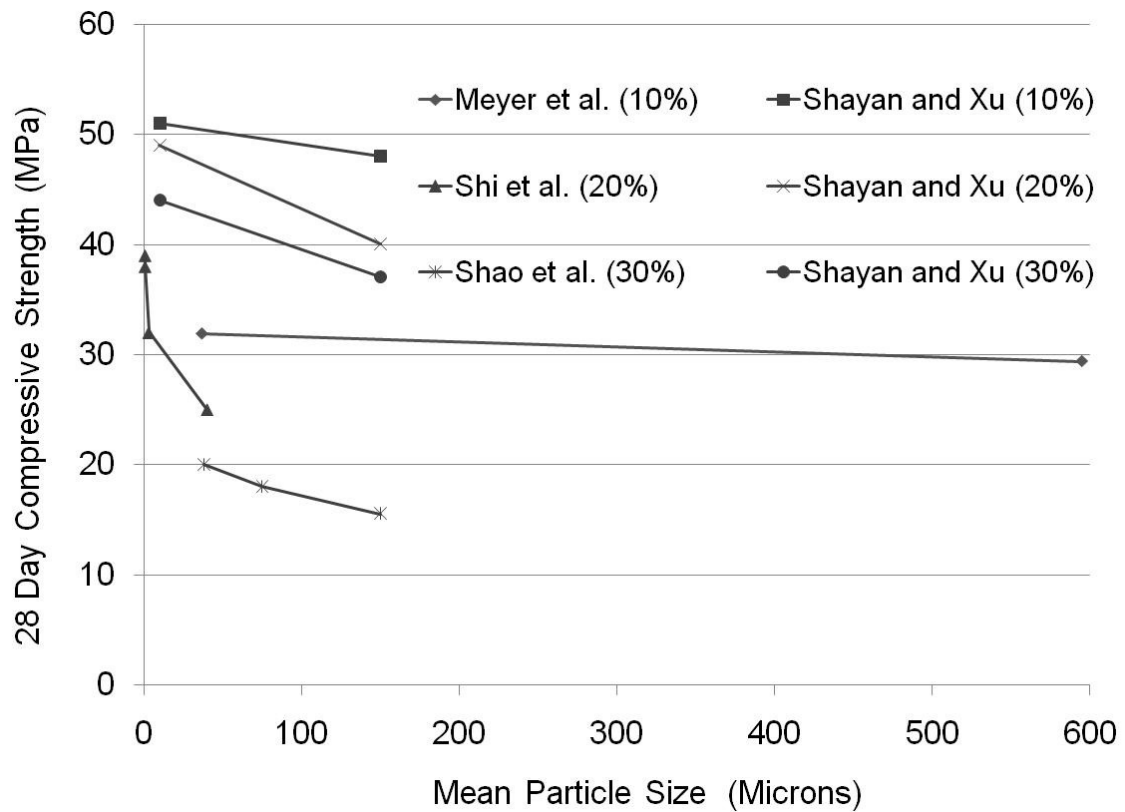


Figure 2.2 28-day compressive strength vs. glass particle size for various percent replacements [14,26]

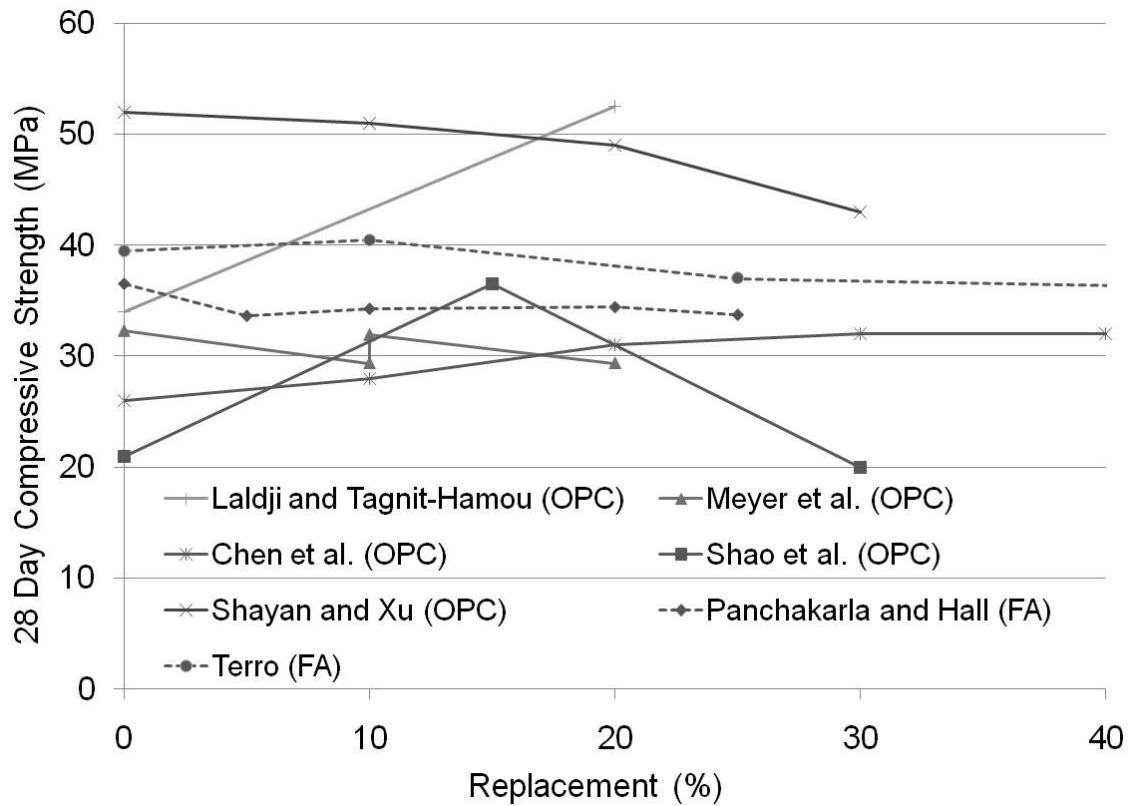


Figure 2.3 28-day compressive strength for various percentages of waste glass replacing OPC and fine aggregate (FA) [7,14,29-33]

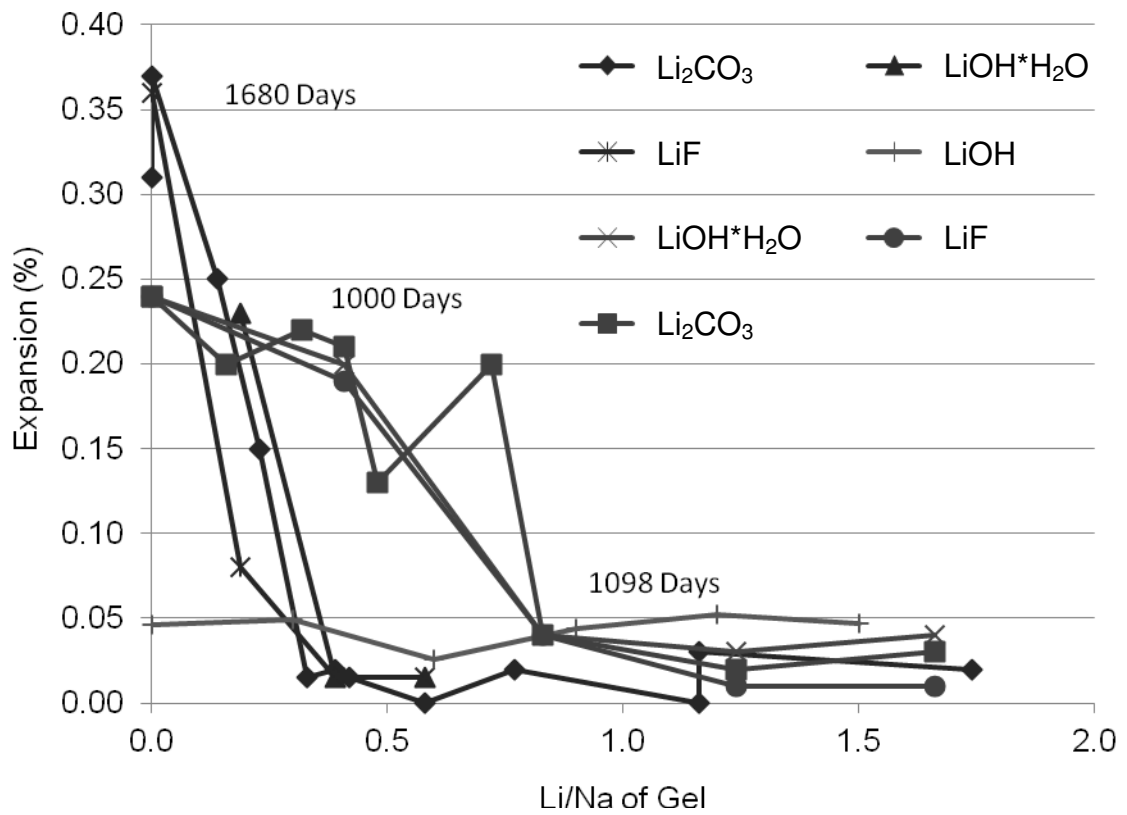


Figure 2.4 Li/Na of gel vs. measured expansion after 1000, 1098, and 1680 days [35,45,46]

Chapter 3 Effects of particle size, grinding, and cement alkalinity on the reactivity of waste glass as a supplementary cementitious material

Federico L. M. & Chidiac S. E. (2013). Effects of particle size, grinding, and cement alkalinity on the reactivity of waste glass as a supplementary cementitious material. *Cement and Concrete Research*, submitted, reference # CEMCON-D-13-00408.

Abstract

Clear glass was mechanically ground to achieve particle size distributions similar to Silica Fume (SF) and Ground Granulated Blast Furnace Slag (GGBFS) to study the effects of particle size on reactivity compared to known Supplementary Cementitious Material (SCM). Two cement powders with different alkali contents were hydrated with 10% SCM or glass. The raw materials were also hydrated to identify any reactivity in water alone. Heat of hydration was tracked using differential thermal analysis, and X-Ray diffraction was employed to identify unique crystalline products as a result of the alkalinity. Waste glass reactivity was significantly improved in LA paste and water when ground to 6.6 μm from 16.5 μm . Waste glass was less reactive than other SCMs at the same particle size. A delayed reaction was observed for the HA mixtures. Both the timing and intensity of the reaction peak heat was influenced by SCM reactivity and cement alkalinity.

Key Words: B. Glass, A. Grinding, A. Calorimetry, D. Pozzolan, D. Alkalis

3.0 Introduction

The use of Supplementary Cementitious Material (SCM) in the concrete industry has allowed for significant reduction in the land filling of materials previously considered to be waste, such as silica fume, fly ash, and blast furnace

slag. These materials can offer beneficial properties when combined with cement to form concrete, such as improved densification and reduced coefficient of diffusion, greater durability and chemical resistance, increased workability and strength, and reduced heat of hydration, to name a few [1 - 4]. In addition to the beneficial properties which may be observed in concrete containing SCMs, there is an environmental benefit. Not only is waste diverted from landfills, but the waste materials used in concrete can offset a portion of the cement powder, which is the most energy intensive portion of concrete and results in significant green house gas emission during its production. Waste materials such as Ground Granulated Blast Furnace Slag (GGBFS), Fly Ash (FA) and Silica Fume (SF) provide strength through a pozzolanic reaction, where amorphous silica and calcium hydroxide ($\text{Ca}(\text{OH})_2$) in pore water react to form a C-S-H like product. In some cases, treatment may be used to enhance the reactivity of the waste material. This treatment can be mechanical, chemical, or thermal. The reactivity of most SCMs can be enhanced through mechanical treatment, where grinding is used to reduce the particle size of the material, increasing the surface area available for reaction [5]. A waste material that has not achieved as much success as an SCM is glass. Although the composition of waste glass is comparable to other SCMs, and it has demonstrated pozzolanic properties at particle sizes below 100 μm [6], the cost associated with processing the glass as well as the variation in properties with decreasing particle size and cement alkalinity has prohibited the acceptance of this product [7]. Previous studies have examined the effect of grinding waste glass on its reactivity as measured by compressive strength [8, 9, 10]; however there are very few studies which use other indicative measures at the micro and material scale to quantify the effect on reactivity of grinding to reduce particle size.

In order to better understand the effects of grinding to reduce particle size on the reactivity of waste glass, calorimetry was used to track the reaction kinetics of two particle sizes of waste glass. The glass was ground to particle size

distributions comparable to common SCMs in order to compare the reactivity of the materials. The reactions were carried out in high and low alkali cement, as well as in water alone. The reaction products were further analyzed using X-Ray Diffraction. The reactivity and resulting observed reaction products are presented here within.

3.1 Experimental Program

3.1.1 Material

Clear, unused glass bottles were crushed manually. The particles were separated into smaller fractions using sieves. To achieve the desired particle size distribution, glass smaller than 250 μm was placed in ring grinder for up to 20 minutes, and then a planetary grinder in iso-2-propanol alcohol for up to 45 hours. The particle size distribution of each material, shown in Figure 3.1 [11], was determined using laser particle size analysis. The smallest particle size obtained using the method of grinding was 0.3 μm . The mean particle size for the fine glass, Glass 1, was 6.6 μm , while the mean particle size for the coarse glass, Glass 2, was 16.5 μm .

3.1.2 Test Method

The composition of the materials, Table 3.1, was determined using X-Ray Fluorescence and the surface area of each material was determined by BET using a Nova 220e Surface Area and Pore Size Analyzer by Quantachrome Instruments. Glass 1 and Glass 2 were obtained from the same source, but were ground to different particle size distributions.

A comparison between the compositional requirements of a natural pozzolan by ASTM C 618-05 [12] and the waste glass used in this study is provided in

Table 2. The glass used in this study meets the compositional requirements for a natural pozzolan.

Calorimetry was performed using a TAM Air Calorimeter at 0.45 water to binder ratio for each initial material, as well as cement paste mixtures with 10% SCM replacement by mass. In total, 6 initial materials and 8 cement paste mixtures were analyzed. The testing was performed in accordance with ASTM C1679-09 [13].

Heat of hydration was measured continuously for at least 6 days. Paste specimens for each mixture were also cast in cylindrical moulds which were demoulded at 24 hours and allowed to cure continuously at 23°C and 95% minimum relative humidity. Samples for XRD analysis were cut from the cylindrical hydrated mixtures at various ages. They were submerged in an excess of iso-2-propanol alcohol for 7 days, with the alcohol replaced after 3 days. The samples were removed from the alcohol and placed in an unheated vacuum oven for 24 hours to remove any excess alcohol, then kept in a vacuum desiccator until the time of testing. An X-Ray Diffraction machine was used to analyze the samples at several ages with a Scintag diffractometer and a copper x-ray tube at 2.2kW and 60kV.

3.2 Experimental Results

3.2.1 Calorimetry

The evolution of heat as a function of hydration time for a period of 6 days for the initial materials is shown in Figure 3.2. The thermal equilibrium time was taken as 60 minutes for all materials and mixtures. Although both cements had similar profiles, the LA cement had a higher peak heat. The GGBFS had a delayed peak at approximately 35 hours. G1, G2 and SF did not display significant heat of reaction with water. The paste mixtures containing GGBFS,

SF, and glass in both types of cement showed profiles similar to the control mixtures of 100% OPC paste. In addition, the LA mixtures all demonstrated a higher peak heat and a secondary reaction shoulder at approximately 19 hours, which can be seen in Figure 3.3.

The shoulder observed in the low alkali mixtures is commonly associated with the conversion of ettringite to monosulfate [14] and according to Bensted, this peak is not often observed in cement with less than 12% C_3A . The C_3A content of the LA cement supplied by the manufacturer is 9.9%. A similar shoulder was observed in the work of Poutos et al. [15], where glass was used to replace aggregate. In this case, since the shoulder occurs for all LA mixtures, it cannot be attributed specifically to the use of waste glass.

The mixtures with SCMs (excluding SF) initially show a lower heat evolution than the control mixtures. The heat evolution relative to the control in Figure 3.4 shows that after 40 hours, the SCMs continue to produce heat at a greater rate than the control LA cement. The SF mixture had a unique profile, where the peak heat release was delayed by 2.45 hours, and was 24.47% greater than the control mixture. The mixtures containing GGBFS and G1 performed similarly in terms of reactivity measured by heat evolution.

The relative heat evolution for HA mixtures in Figure 3.5 shows a similar trend, however the SCM mixtures are generally less reactive in the HA cement paste than in LA cement paste. In the HA cement mixtures, GGBFS and G2 performed similarly in terms of reactivity. Mixtures containing G1 appear less reactive in HA cement than in LA cement.

3.2.2 X-Ray Diffraction

In order to identify any unique phases present due to the different particle sizes, alkalinities, and rates of reaction, X-Ray Diffraction was performed on the hydrated mixtures at 28 days. A comparison of the diffraction patterns for all 10

mixtures is given in Figure 3.6, with major constituents in the pattern identified [16, 17]. Results show that the patterns are similar for the mixtures containing fine and coarse glass for each cement type, however when the two cement types are compared, slight differences are observed. The HA cement displays a greater signal of ettringite and syngenite for both glass sizes. Therefore, any differences in the resulting crystalline phases is more likely a result of the higher alkalinity, which is known to promote syngenite formation [18, 19], than the difference in particle size or reactivity as a result of grinding. The high concentration of potassium in the HA cement initiates the syngenite and can also lead to a decrease in the pH of the pore solution [20], which in turn can delay the dissolution of silica and the pozzolanic reaction in general. In Figure 3.3, both the initial peak heat and the total overall heat evolution for the HA mixtures are retarded when compared to the LA mixtures. In the HA mixtures, there is a lack of the shoulder at 19 hours hydration observed for the LA mixtures, which is associated with ettringite conversion. The presence of excess syngenite in the HA cement results in prevention of the conversion from ettringite to monosulphate [21].

3.3 Discussion

The rate of heat evolution for a hydrating cement containing SCM is known to differ from that of pure OPC. For cement containing waste glass, the rate of heat evolution decreases as the amount of waste glass increases [22]. In general, there is a competition between at least two mechanisms which influence heat of hydration when SCMs are used [23]. There is a dilution effect, where the replacement of a percentage of the cement results in a reduction in the peak heat of hydration. In this work, a comparison of mixtures with the same dilution rate removes the influence of this effect when the mixtures are compared. The second mechanism is pozzolanic activity, which may add to the total long term heat of

hydration after the peak temperature of reaction has occurred. The pozzolanic effect of each SCM is evident in the additional heat of hydration after 40 hours of reaction for both cements.

Although it is difficult to directly track the heat of hydration from pozzolanic reactivity, its influence can be observed comparatively. It is prudent to identify the factors which influence the pozzolanic reaction in the system; particle size of the pozzolanic material, percent addition of the pozzolanic material, and alkalinity of the cement powder. The particle size of the pozzolan is one factor which is known to affect its reactivity and therefore the hydration of the system. A decreased particle size leads to an increase in surface area, where surface area can be more influential than percent addition on pozzolan reactivity [24].

When other SCMs such as cement kiln dust and fly ash were ground to improve reactivity, it was observed that both the regime of grinding and the grinding time influenced the final reactivity. The increase in reactivity was traced to a decrease in crystallinity brought on by grinding [25]. However; when the particle size of waste glass is decreased by a factor of 10 through grinding, the reactivity is seen to improve when hydration occurs in water and in LA cement. In HA cement, the amount of grinding did not significantly alter the reactivity of the glass. XRD of both glasses did not reveal a distinct or measurable difference in crystallinity as a result of increased grinding.

When compared to other SCMs, grinding glass to a similar particle size was not sufficient to match reactivity. In the case of SF, it was not possible to mechanically grind the glass to a representative size for comparison. When ground to the same size as GGBFS; glass was less reactive in LA cement and equally as reactive in HA cement.

Ultimately, the reactivity of a cementitious or pozzolanic material is thought to depend on the rate of silica release, and since silica dissolution is a function of the surface area and therefore particle size of the material, it follows that a reduction in particle size would directly influence reactivity [26]. Silica release is

also controlled by the pH of the pore solution, where a higher pH results in a greater rate of silica dissolution. The observation of syngenite in the HA mixtures may indicate an alteration of the pH of the system. This lowered pH would delay the dissolution of silica from the SCM, and allow hydration of high calcium C-S-H to take place. The lack of conversion of ettringite to monosulphate and the increased syngenite observed in the XRD of the HA paste mixtures provides some evidence that there is a temporary pH effect in the HA cement mixtures. Once the syngenite has changed phase and the pH has risen, there may be other factors such as diffusion of silica, calcium and other alkali ions retarding pozzolanic reaction in the HA mixtures that the described experimental program was unable to capture. The alkalinity of the cement is therefore an important consideration with respect to reactivity, and from the results presented here, may be as influential as particle size.

3.4 Conclusions

Based on the results presented in this paper from laboratory experimentation with traditional SCM and waste glass in cement paste, the following conclusions can be made:

- Grinding improves the reactivity of waste glass in LA cement.
- A glass with a mean particle size of 16.5 μm does not possess notable reactivity in cement, but that with a mean particle size of 6.6 μm does.
- Grinding waste glass to the same particle size as other SCMs such as SF and GGBFS does not result in equivalent reactivity.
- At particle sizes between 6.6 μm and 16.5 μm alkalinity is more influential than surface area on the pozzolanic reactivity of glass in cement.
- The appearance of syngenite may be responsible for delaying the reactivity of the HA mixtures by temporarily lowering the pH and slowing silica dissolution from the SCMs.

Acknowledgements

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References

- [1] J. Daube, R. Bakker, Portland blast-furnace slag cement: a review, in: G. Frohnsdorff (Ed.), Blended Cement, ASTM STP 892, ASTM International, West Conshohocken, 1986, pp. 5-14.
- [2] P. K. Mehta, Condensed silica fume, in: R. N. Swamy (Ed.), Cement Replacement Materials, Surrey University Press, Glasgow, 1986, pp. 134-170.
- [3] P. L. Maier, S. A. Durham, Beneficial use of recycled materials in concrete mixtures, *Const. Build. Mater.* 29 (2012) 428-437.
- [4] R. Bleszynski, R. D. Hooton, M. D. A. Thomas, C. A. Rogers, Durability of ternary blend concrete with silica fume and blast-furnace slag: laboratory and outdoor exposure site studies, *ACI Mater. J.* 99 (2002) 499-508.
- [5] V. M. Malhotra, P. K. Mehta, Pozzolanic and Cementitious Materials (Advances In Concrete Technology), Gordon and Breach Publishers, New York, 1996, pp. 5-39.
- [6] C. Shi, Y. Wu, C. Riefler, H. Wang, Characteristics and pozzolanic reactivity of glass powders, *Cem. Concr. Res.* 35 (2005) 987-993.
- [7] W. Jin, Alkali-Silica Reaction in Concrete with Glass Aggregate-A Chemo-physico-mechanical Approach, PhD Thesis, Columbia University, New York, 1998.

- [8] Y. Shao, T. Lefort, S. Moras, D. Rodriguez, Studies on concrete containing ground waste glass, *Cem. Concr. Res.* 30 (2000) 91-100.
- [9] C. H. Chen, R. Huang, J. K. Wu, C. C. Yang, Waste e-glass particles used in cementitious mixtures, *Cem. Concr. Res.* 36 (2006) 449-456.
- [10] L. A. Pereira de Oliveira, J. P. Castro Gomes, P. Santos, Optimization of pozzolanic reaction of ground waste glass incorporated in cement mortars, in L. Braganca (Ed.), *SB07 Sustainable Construction, Materials and Practices: Challenge of the Industry for the New Millennium*, IOS Press, Amsterdam, 2007, pp.928-934.
- [11] L. M. Federico, S. E. Chidiac, L. Raki, Reactivity of cement mixtures containing waste glass using thermal analysis, *J. Therm. Anal. Calorim.* 104 (2011) 849-858.
- [12] ASTM Standard C 618, Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete, ASTM International, West Conshohocken, 2005.
- [13] ASTM Standard C 1679, Standard Practice for Measuring Hydration Kineticsof Hydraulic Cementitious Mixtures Using Isothermal Calorimetry, ASTM International, West Conshohocken, 2009.
- [14] J. Bensted, Some applications of conduction calorimetry to cement hydration, *Adv. Cem. Res.* 1 (1987) 35-44.
- [15] K. H. Poutos, A. M. Alani, P. J. Walden, C. M. Sangha, Relative temperature changes within concrete made with recycled glass aggregate, *Constr. Build. Mater.* 22 (2008) 557-565.
- [16] P. E. Stutzman, Guide for X-Ray Powder Diffraction Analysis of Portland Cement and Clinker, National Institute of Standards and Technology, Gaithersburg, 1996.
- [17] B. El Elaoui, M. Benkaddour, Hydration of C_3A in the presence of $CaCO_3$, *J. Therm. Anal.* 48 (1997) 893-901.

- [18] J. Stark, K. Bollmann, Delayed Ettringite Formation in Concrete, Nordic Concrete Research, NCR, Meeting, Tech. Committee of NCR, Oslo, 1999, pp.4-28.
- [19] B. Samet, S. L. Sarker, The influence of calcium sulfate form on the initial hydration of clinkers containing different alkali combinations, *Cem. Concr. Res.* 27 (1997) 369-380.
- [20] M. S. Konsta-Gdoutos, S. P. Shah, Hydration and properties of novel blended cements based on cement kiln dust and blast furnace slag, *Cem. Concr. Res.* 33 (2003) 1269-1276.
- [21] C. J. Warren, E. J. Reardon, The solubility of ettringite at 25 °C, *Cem. Concr. Res.* 24 (1994) 1515-1524.
- [22] T. D. Dyer, R. K. Dhir, Chemical reactions of glass cullet used as cement component, *J. Mater. Civ. Eng.* 13 (2001) 412-417.
- [23] N. Y. Mostafa, P. W. Brown, Heat of hydration of high reactive pozzolans in blended cements: Isothermal conduction calorimetry, *Thermochim. Acta*, 435 (2005) 162-167.
- [24] H. Binici, O. Aksogan, I. H. Gagatay, M. Tokyay, E. Emsen, The effect of particle size distribution on the properties of blended cements incorporating GGBFS and natural pozzolan (NP), *Powder Technol.* 177 (2007) 140-147.
- [25] J. Ryou, S. P. Shah, M. S. Konsta-Gdoutos, Recycling of cement industry wastes by grinding process, *Adv. Appl. Ceram.* 105 (2006) 274-279.
- [26] A. Carles-Gibergues, M. Cyr, M. Moisson, E. Ringot, A simple way to mitigate alkali-silica reaction, *Mater. Struct.* 41 (2008) 73-83.

Table 3.1 Chemical composition and surface area of materials

(%)	Low Alkali	High Alkali	Silica Fume	GGBFS	Glass 1	Glass 2
SiO ₂	20.41	19.65	94.90	35.85	71.59	72.06
TiO ₂	0.32	0.24	< 0.01	0.59	0.02	0.03
Al ₂ O ₃	5.54	5.56	< 0.01	10.52	1.78	1.81
Fe ₂ O ₃	2.33	2.61	0.05	0.67	0.13	0.07
CaO	65.06	64.32	0.40	36.74	10.73	10.81
MgO	3.33	2.54	0.66	12.74	0.18	0.21
MnO	0.07	0.04	0.04	0.57	< 0.01	< 0.01
Na ₂ O	0.28	0.20	0.01	0.42	13.01	13.50
K ₂ O	0.24	0.79	0.63	0.47	0.40	0.40
LOI	2.19	3.46	3.01	1.23	2.32	1.00
Na ₂ O Eq.	0.44	0.72	0.42	0.73	13.27	13.76
Surface Area m ² /g	1.99	2.57	20.67	1.82	2.32	1.59

Table 3.2 Comparison of ASTM C 618-05 natural pozzolan requirements and waste glass composition

	Requirement for Natural Pozzolan	Average Waste Glass Composition
SiO ₂ plus Al ₂ O ₃ plus Fe ₂ O ₃ , min %	70.00	73.72
SO ₃ , max %	4.00	-
Moisture Content, max %	3.00	-
LOI, max %	10.00	1.66

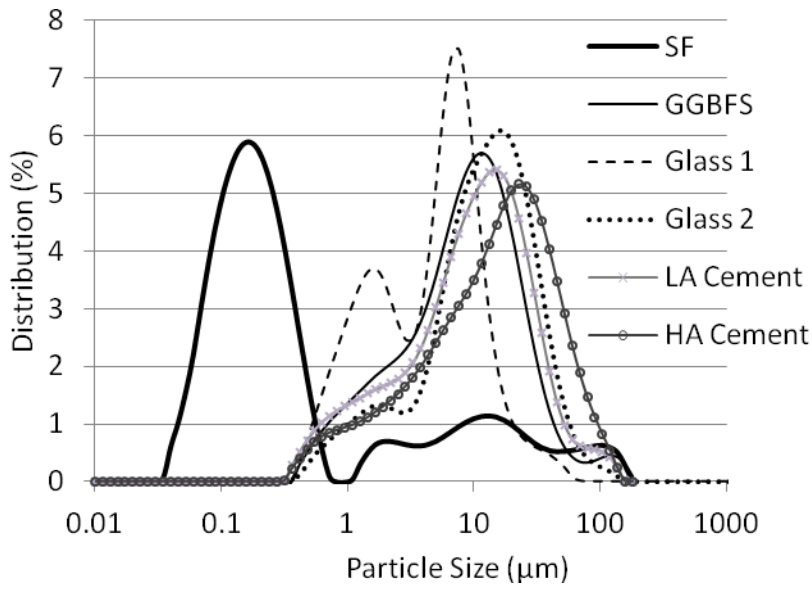


Figure 3.1 Particle size distribution of glass, SCMs, low alkali and high alkali cement

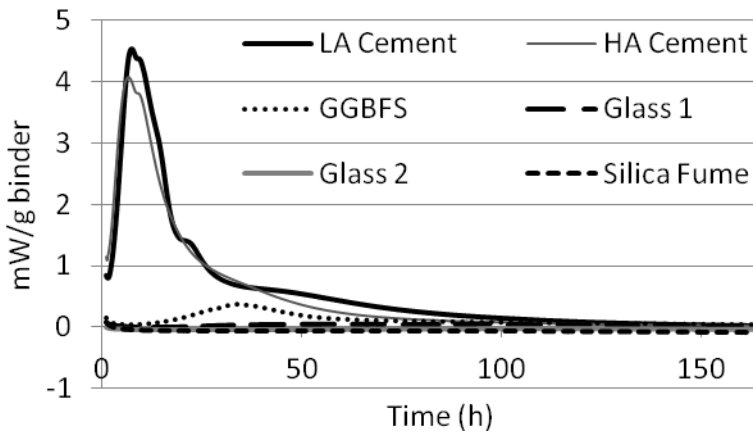


Figure 3.2 Heat of hydration of initial materials in water/binder = 0.45

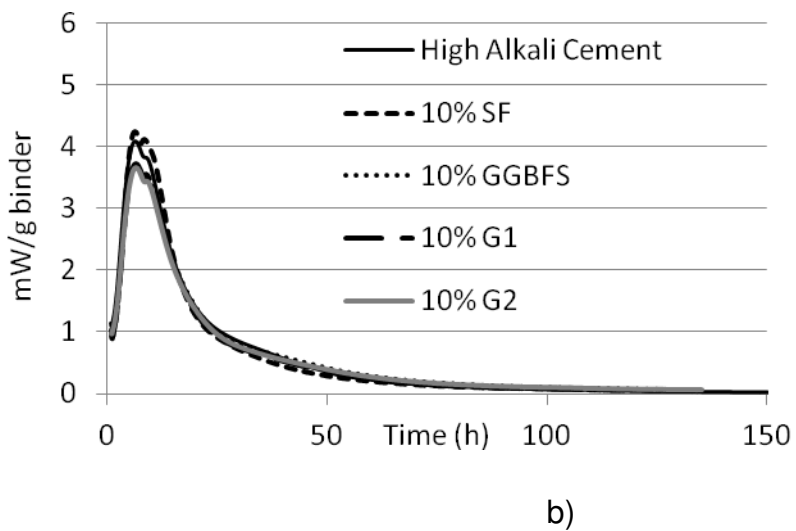
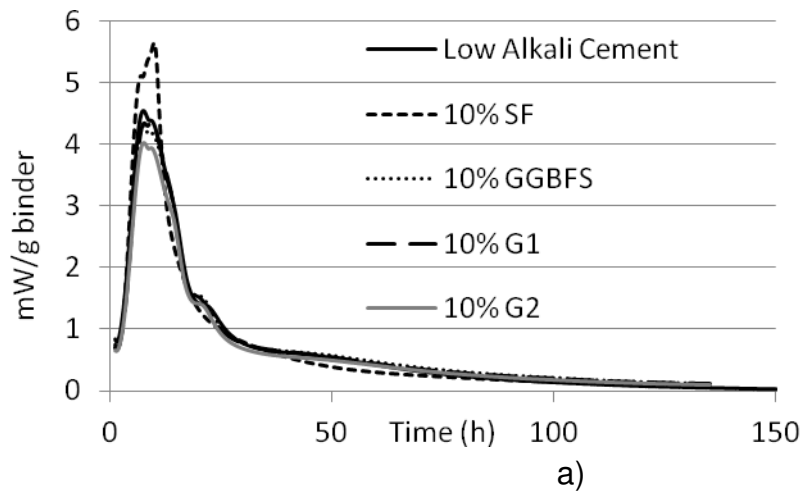


Figure 3.3 Heat evolution for a) low alkali and b) high alkali cement mixtures with various supplementary cementitious materials

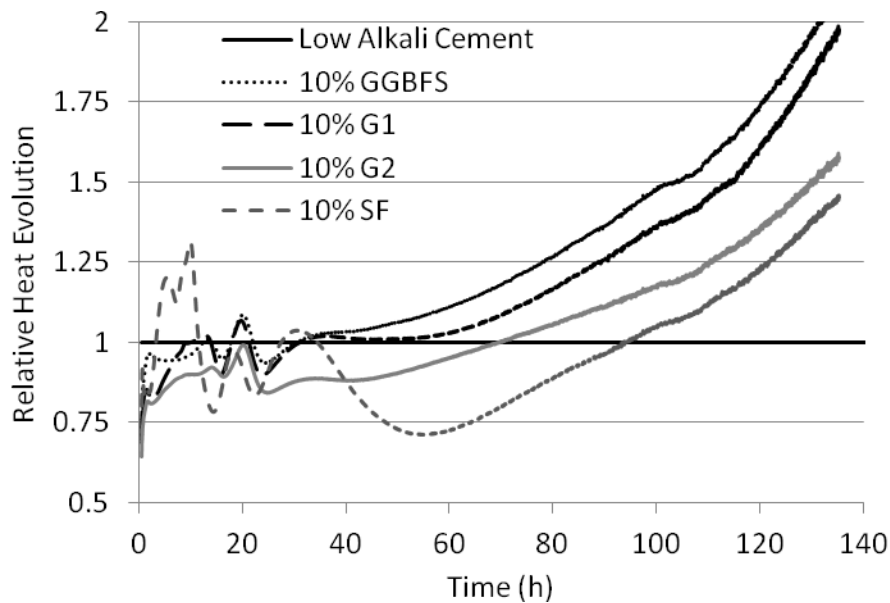


Figure 3.4 Relative heat of hydration for low alkali cement with 10% SCM replacement

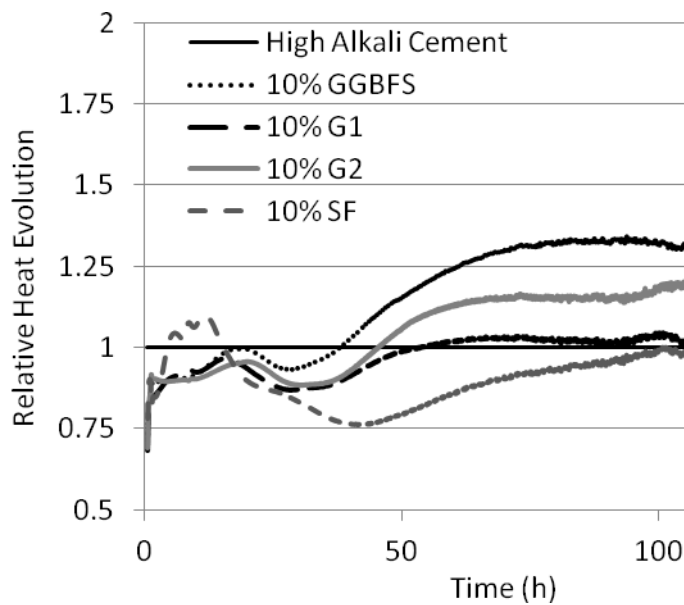


Figure 3.5 Relative heat of hydration for high alkali cement with 10% SCM replacement

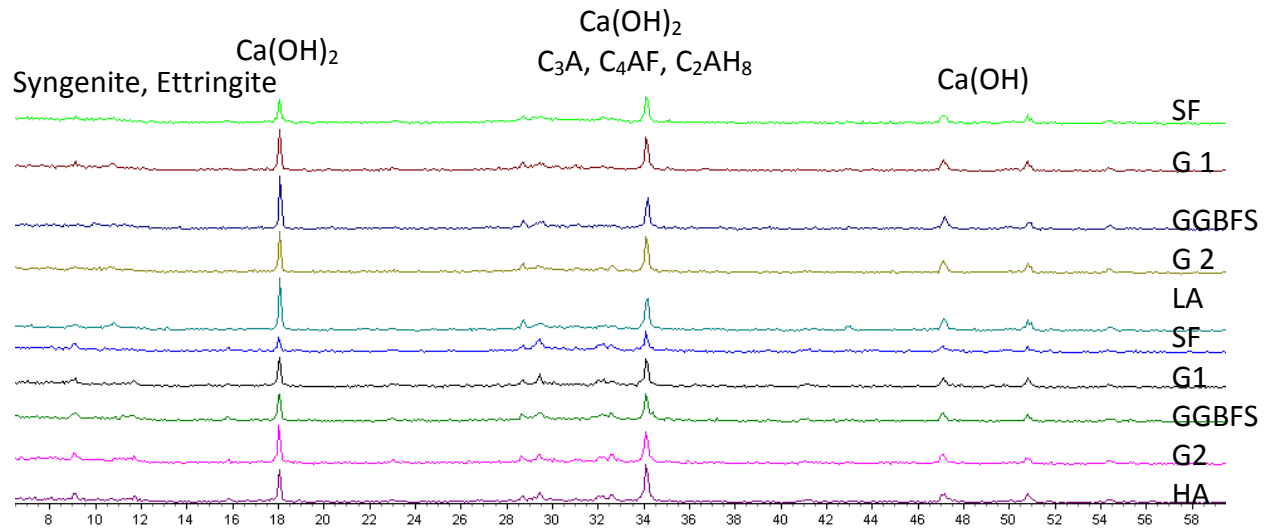


Figure 3.6 XRD pattern for all mixtures, 10% replacement of cement with SCM, at 28 days hydration

Chapter 4 Reactivity of cement mixtures containing waste glass using thermal analysis

Federico L. M., Chidiac S. E., & Raki L. (2011). Reactivity of cement mixtures containing waste glass using thermal analysis, *Journal of Thermal Analysis and Calorimetry*, 104(3), 849-858.

Abstract

A laboratory study was undertaken to compare the performance of waste glass as a Supplementary Cementitious Material (SCM) to traditional SCMs at the same particle size and level of replacement in both high and low alkali cement paste. The consumption of $\text{Ca}(\text{OH})_2$ as measured by differential thermal analysis (DTA) is used as an indicator of reactivity. The DTA results of the pastes aged to 150 days are presented, and indicate that glass reactivity is similar to ground granulated blast furnace slag (GGBFS) and lower than silica fume (SF) at comparable particle sizes. Alkali-silica reaction (ASR) is not present for particle sizes below 100 μm , but is induced by agglomeration of the glass particles and is observed by fluorescence in optical microscopy images. Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS) are used to compare the microstructural properties of the SCMs and measure the chemical composition of the reaction products. The alkalinity of the cement was found to influence the nature of composition as observed by thermal analysis, and the temperatures at which their reactions occurred.

Key Words: SCM, ASR, pozzolan, waste glass, DTA, alkalinity

4.0 Introduction

Supplementary cementitious materials are used as cement replacement in concrete to improve a number of concrete properties, including durability, ultimate strength, workability, heat of hydration and permeability [1-4]. These properties are developed through pozzolanic reaction between amorphous silica in the SCMs and Portlandite, $(\text{Ca}(\text{OH})_2)$, released during cement hydration and formation of insoluble calcium silicate hydrates (C-S-H) [5].

Waste-based and industry by-product SCMs, such as SF and GGBFS, can also offset a portion of greenhouse gas (GHG) emissions that would result from the production of an equivalent amount of Portland cement from raw materials. For each tonne of Portland cement powder produced, a nearly equivalent amount of GHG is produced [3]. In 2001, the Canadian production of GHG per tonne of cement was 0.8 tonnes, which is similar to the 1996 value [6], and so there is still significant opportunity for environmental improvement.

Other potential SCMs include natural products, domestic, industrial and agricultural waste sources, and demolition waste [7]. A post-consumer waste material which has yet to achieve the status of a commonplace SCM is bottle glass. This material is collected in municipal waste streams, and although glass is highly recyclable, the mixing of broken pieces can result in a reduction in the value of the waste product, as it cannot be separated by colour once this level of mixing has occurred. For this reason, recycled glass often ends up in low value products, or else in a landfill [8-10]. The use of waste glass as a partial cement replacement is not new [11,12] and a number of studies have explored different uses for it in concrete. However, it has yet to become a competitive product in the marketplace due to many early reported challenges associated with its use. Some of these challenges include the production of an Alkali-silica reaction (ASR) gel in the presence of large particles of glass, the loss of early strength

due to contamination [13], and the cost associated with processing and grinding waste glass [12].

The effects of particle size on reactivity of pozzolanic SCMs and glass has been demonstrated [14, 15], where increased fineness led to an increase in early age compressive strength, even in the absence of activators. In some cases, the compressive strength of mortar bars made with glass powder as an SCM demonstrated a higher compressive strength than those made with an equivalent amount of fly ash [9, 16, 17]. Particle size is also influential in controlling the mechanism between alkali-silica and pozzolanic reactions. For glass particles with sizes below 300 μm , an ASR gel is less likely to be produced than with aggregate sized particles, while particle sizes below 75 μm often demonstrate a pozzolanic reactivity according to the literature [10, 13, 18]. This general trend is not consistent, and depending on the composition of the glassy material, ASR can be exhibited even at very small particle sizes [19]. In other studies a pessimum particle size was identified, where the maximum ASR expansion occurred at an intermediate particle size depending on the reactivity of the material [20,21]. Both the reactivity of glass and its resulting reaction products have also been closely related to its chemical composition [22].

The pozzolanic and alkali-silica reactions follow similar mechanisms. Specifically, both require the dissolution of amorphous silica in an alkaline solution followed by the formation of a product bearing calcium, silica, and alkali ions. The main difference between the two reactions is the properties of the resulting products, which can be loosely related to their chemical composition, namely the ratio of alkali to calcium and calcium to silica [23]. In a different study, a theory on the relationship between the chemical composition of the product and particle size of the waste glass suggested that the difference between ASR and pozzolanic products is conditioned by the particle size of the glass, but the controlling mechanism is unknown [24].

The goals of the current paper are to determine whether or not waste glass would be comparatively reactive if ground to the same particle size as currently accepted SCMs, to determine the nature of the reaction, i.e. pozzolanic versus ASR, and to investigate the effect of cement alkalinity on the reactivity of the mixture.

4.1 Experimental

Six cementing powders were studied in this investigation. They included high alkali cement (HA), low alkali cement (LA), SF, GGBFS, and glass powder. The composition of all raw materials was determined by X-ray fluorescence. The two cement powders were obtained from Lafarge North America with the composition shown in Table 4.1. The low alkali cement has a total Na_2O equivalence of 0.44 %, and for the high alkali cement the Na_2O equivalence is 0.72 %. SF from Norchem and GGBFS from Lafarge North America were obtained to serve as reference SCMs with distinctly different particle sizes.

Clear, unused wine bottles were the source of the glass. The glass was crushed by hand initially then further ground using a planetary grinder and a ring grinder to obtain two particle size distributions. The first, Glass 1, was intended to have a particle size distribution comparable to that of the SF, and the second, Glass 2, to that of the GGBFS. The particle size distributions of the SCMs and glasses are shown in Figure 4.1. Although it was not possible to produce glass particles as fine as those of SF by grinding, a factor of nearly 10 was achieved to separate the glass meant to represent GGBFS from that of SF. Accordingly, the performance of the two glass groups was expected to be different. The mean particle size of Glass 1 and Glass 2 was 6.6 μm and 16.5 μm , respectively.

A Hitachi S-4800 Scanning Electron Microscope was used to evaluate the microstructure of the materials. Surface area for each sample was measured using the BET technique with a Nova 220e Surface Area and Pore Size Analyzer

from Quantachrome Instruments. The surface areas, which are given in Table 4.2 reveal that glass at a comparable particle size has a lower surface area than GGBFS, and a much lower surface area than SF. These results indicate that the shape of the glass particles differs from those of GGBFS and SF.

The SEM images, shown in Figure 4.2, are representative of the cementing materials. Glass 1, shown in Figure 4.2b, was ground to simulate SF, Figure 4.2a, but has more surface characteristics in common with GGBFS, Figure 4.2c. The fine glass and GGBF both share a combination of angular particles and foiled particles. The particles in Glass 2, shown in Figure 4.2d, have a more consistent angular shape, and although they are similar in particle size distribution to GGBFS, they are not similar in particle shape and surface characteristics since there are no apparent foiled particles. The lower surface area of Glass 2 is most likely due to the absence of the foiled particles seen in the GGBFS. These foiled particles would have a higher surface area than the relatively smooth and regularly angled particles observed for Glass 2, and therefore their absence in the glass may result in a lower surface area for similar particle size distributions.

Cement paste specimens were prepared by replacing 10 % by mass of either LA or HA cement with SF, GGBFS, Glass 1, or Glass 2. The 10 % replacement of waste glass is based on previous evidence which indicates that this is an optimum percent cement replacement in order to maintain or improve compressive strength [10,17,24]. A control mixture of 100 % cement was also made for a total of 10 mixtures, Table 4.3. Each mixture was made with a water/binder ratio of 0.45 and cast into 100 mm long cylindrical plastic moulds, with diameters of 35 mm. The freshly cast mixtures were capped to prevent moisture loss and allowed to hydrate for 24 hours before the moulds were removed. The specimens were stored at 23 °C and 95 % minimum relative humidity until hydration was stopped at predetermined time intervals.

Samples from each mixture were freeze-dried to stop hydration with vacuum pumping while submerged in liquid nitrogen for 24 hours, followed by 24 hours drying in an unheated vacuum oven. While being stored for testing, mixture samples were sealed in a desiccator. Carbonation of the samples in the form of CaCO_3 was generally below 2.0 % for low alkali mixtures and below 3.3 % for high alkali mixtures. Simultaneous DTA was performed on crushed samples using a TA Q600 in nitrogen gas at 100 ml/min flow rate, with a ramping rate of 10 °C/min from room temperature to 1000 °C in an alumina pan. Sample size was 35 ± 5 mg. Each mixture was tested at 1, 14, 28, 91, and 150 days.

4.2 Data Analysis

Thermal analysis results and trend lines are presented in Figures 4.3-4.5. The Ca(OH)_2 content was measured at different times as a percentage of the total sample mass, as shown in Figure 4.3. By replacing 10 % of the cement in each mixture with a SCM, 10% of the Ca(OH)_2 which would be produced during the hydration of Portland cement has been effectively removed. When the amount of Ca(OH)_2 in a mixture is measured to be less than 10 % of the control, the additional consumption of Ca(OH)_2 can be attributed to another chemical reaction. A comparison of the mass loss to the original cement content (Figure 4.4) shows that the low alkali mixtures have higher levels of Ca(OH)_2 than the equivalent high alkali mixture at the same age.

Figure 4.5 shows the relative Ca(OH)_2 consumption for all mixtures. At 28 days, only the mixtures containing SF have consumed significant amounts of Ca(OH)_2 , while the other mixtures actually show increased amounts of Ca(OH)_2 . This increase is expected as a result of the increased level of hydration from a higher relative water/cement ratio at the given water/ binder ratio when SCMs replace a portion of the cement [25]. At 91 days, all mixtures have a reduced Ca(OH)_2 content below 90 % of the control, but at 150 days, the levels of

Ca(OH)_2 in the low alkali mixtures have increased. The high alkali mixtures generally maintain the same level of Ca(OH)_2 after 91 days. At early ages, all mixtures, except for those with SF, are experiencing hydration, leading to the increase in Ca(OH)_2 , while at 90 days, Ca(OH)_2 is being consumed at a rate greater than that at which it is being produced by the hydration reaction. In the low alkali mixtures, the Ca(OH)_2 level recovers at 150 days. The production of Ca(OH)_2 from hydration or another source is taking place. Since typically Portland cement has reached 85 % hydration by 100 days [26], the additional Ca(OH)_2 is unlikely to be a result of continued hydration.

The temperature ranges for each phase from the literature [27-35] were used to compare the thermogravimetric results at each age. Figure 4.6 shows the differential thermal analysis of the mixtures at 28 days. It is apparent that certain phases are present only in low alkali mixtures, such as the phase between 165 °C and 175 °C, which is most likely ettringite at early ages and AFm or C_3AH_6 as hydration continues [36]. The phase located between 260 °C and 280 °C is also found only in the low alkali mixtures, which is another form of calcium aluminate hydrate, most likely cubic C_3AH_6 or C_4AH_{13} [36]. The temperature at which the Ca(OH)_2 peak occurs is lower for the high alkali mixtures. At 28 days the average temperature at which the Ca(OH)_2 peak occurs for the low alkali mixtures is 448 °C, while for the high alkali mixtures, the average temperature is 444 °C. The peak which occurs between 650 °C and 750 °C is due to the decomposition of Calcium Carbonate (CaCO_3). Unlike the Ca(OH)_2 , the CaCO_3 peak occurs at a higher average temperature (692 °C) for the high alkali mixtures than for the low alkali mixtures (676 °C).

Grain size can affect the temperature at which the peak occurs, where the peak temperature decreases as the crystal grain size decreases [37]. If higher alkalinity results in more but smaller Ca(OH)_2 crystals, this would account for the observed temperature differences between the Ca(OH)_2 peak in high and low alkali mixtures.

The decrease in the amount of $\text{Ca}(\text{OH})_2$ observed in the thermogravimetric analysis can be at least partially attributed to one or both of two reactions, namely alkali silica reaction (ASR) and pozzolanic reaction. Both reactions consume $\text{Ca}(\text{OH})_2$ and reactive silica to produce chemically similar products with very different physical characteristics. In determining which reaction is consuming $\text{Ca}(\text{OH})_2$, a sample from each mixture was tested for the presence of ASR using the uranyl acetate staining method [38] according to ASTM C856 [39]. Freshly cut samples were exposed to uranyl acetate and observed under ultraviolet light with an optical microscope at 79 and 152 days. No fluorescence indicative of ASR was observed for control mixtures, mixtures containing GGBFS, SF, or Glass 2 (coarse glass). Mixtures containing Glass 1 (mixture 2 and mixture 7) demonstrated fluorescence and well defined reaction rims at locations where fine glass was agglomerated together as a result of the grinding process. Some agglomerates, especially those which demonstrated fluorescence, experienced drying cracks typically associated with ASR. The location of the agglomerate did not appear to influence its characteristics, as several agglomerates with distinctly different properties were often observed in close proximity.

Some agglomerates of glass did not demonstrate fluorescence. In order to understand why some agglomerates would fluoresce and some would not, a more detailed analysis was performed and the composition of agglomerates ranging in size, colour, and level of fluorescence was examined using Energy Dispersive X-Ray Spectroscopy (EDS). The agglomerates were observed to range in diameter from approximately 25 μm to 2500 μm and to vary in colour from bright white to very dark grey under optical microscopy, and reaction rims were evident around most particles, as shown in Figure 4.7.

The trend in both low and high alkali mixtures was that very small agglomerates, with an approximate area less than 0.01 μm^2 , were more likely to fluoresce under UV light than larger agglomerates. Between 0.01 μm^2 and 0.1 μm^2 , agglomerates were less likely to fluoresce. At an area greater than 0.1 μm^2 ,

agglomerates were just as likely to fluoresce as not to. The presence of this change in behaviour at intermediate sizes suggests that there is more than one process controlling the reaction of the agglomerate and the resulting product, similar to the pessimum effect of size observed in the literature [20, 40].

A typical Ca/Si ratio for ASR is 0.01-1.0 [41-44], and for C-S-H it is 1.5-2.0 [31, 45]. The glass used in the mixtures had a Ca/Si = 0.15, and a Na₂O equivalent of 13.27%. Table 4.4 shows the range and average composition at various locations in and around the agglomerates in mixtures 2 and 7. Within the agglomerates, the Ca/Si ratio was similar for both low alkali and high alkali mixtures. There was variability in the paste compositions for both mixtures near and away from the agglomerate. In general, as distance from the agglomerate increased, so did calcium content, while alkali content was variable. The silica content in the paste was significantly lower than in the agglomerates.

For the high alkali mixture, the centre gel and rim gel are compositionally comparable to ASR. The paste has a high Ca/Si ratio, and the Ca/Si ratio of the rim paste is much higher than that of the low alkali mixture. It is closer to C-S-H than ASR. ASR typically has a higher ratio of alkalis/Ca. The results in the table support the identification of ASR like material in all low alkali gel sites and in the centre and rim gel of the high alkali mixture.

In order to assess the cause of the variation in colours of the agglomerates, the compositions are compared in Figure 4.8. Light agglomerates have Ca/Si ratios ranging from zero all the way to those typical of C-S-H (1.5-2), but also have alkali levels higher than would be expected in C-S-H. The medium and dark agglomerates demonstrate Ca/Si ratios and alkali contents of a low calcium C-S-H material similar to that observed in agglomerates of SF in other work [45]. The agglomerates with different coloured centers and rims show a composition which combines that of the light and dark agglomerates.

The colour of the agglomerates is loosely related to the tendency of the agglomerates to fluoresce under UV light when treated with uranyl acetate. Most

agglomerates that fluoresced were light in colour, however being light in colour did not necessarily mean that fluorescing would occur, as many light agglomerates did not fluoresce. No dark agglomerates fluoresced; however fluorescing did sometimes occur in the light reaction rim surrounding dark agglomerates. Medium coloured agglomerates and those which were light with a dark rim were just as likely to fluoresce as not, however no fluorescence occurred in dark rims.

From Figure 4.9, agglomerates which demonstrated fluorescing had a lower Ca/Si ratio everywhere but in the gel side of the reaction rim. When slight fluorescence was observed, the composition at all locations was similar to the agglomerates that fluoresced but with slightly more calcium and more alkalis. When fluorescence was observed in the reaction rim, the alkali content was very high in the gel and rim, while Ca/Si was very high outside of the agglomerate, with very low alkali content. When no fluorescence was observed, the gel composition had only slightly higher Ca/Si and slightly lower alkali/Ca than the gel that fluoresced. The outer reaction rim and paste has a consistently high Ca/Si and low alkali/Ca when no fluorescence occurred.

4.3 Discussion

Although the glass was ground to achieve a particle size comparable to GGBFS and SF, the surface areas of the particles were different. This is especially true for SF, where the surface area was nearly ten times greater than that of the glass at the smallest particle size achievable through the grinding methods used. Mixtures composed of particles whose size is the smallest and surface area is the largest have the largest consumption of $\text{Ca}(\text{OH})_2$ for all materials in both low and high alkali cement. This trend is well documented in the literature [46-50]. The observed formation of ASR in mixtures containing fine glass is due to the agglomeration of particles and not due to the particle size.

Agglomeration of particles represents a high localized concentration of glass in comparison to the rest of the mixture. In areas where the glass was well distributed and in mixtures containing GGBFS, SF, or coarse glass, no ASR gel formation was observed.

Although ASR occurred only at the location of glass agglomerates, it occurred regardless of the alkalinity of the cement. When ASR was observed, it occurred only in the vicinity of the agglomerates, and was not detected throughout the paste. Therefore for a particle size distribution between 0.3 μm and 100 μm , ASR does not occur, and pozzolanic reaction takes place. At an agglomerate size ranging in area from 0.01-0.26 μm^2 , ASR is found to occur in agglomerates, but is not guaranteed.

Upon further investigation, the agglomerates of varying sizes were found to have unique properties in terms of colour, fluorescence, and composition, which were not easily related to one another. Each colour of agglomerate observed has a unique composition. Those which were darker and less likely to fluoresce had lower alkali content and a Ca/Si ratio similar to low calcium C-S-H. Those which were lighter and more likely to fluoresce had higher alkali contents, especially when fluorescing occurred only in the reaction rim. In low alkali cement mixtures, for which less data was obtained, the centre gel and reaction rims were compositionally similar to ASR, and the alkali content was generally mid range, decreasing towards the paste. In high alkali mixtures, a more distinct composition of ASR was observed in the interior reaction products and C-S-H in the outer rim and paste. The alkali content was much higher within the agglomerate, but was comparable to low alkali mixtures in the paste. The composition of the reaction rim not only influenced its colour and fluorescence, but that of the surrounding material. It is obvious from the results that calcium is being transported from the hydrating cement into the glass agglomerate, and alkalis are being relocated both throughout the gel and into the reaction rim. There are examples of agglomerates which seem to experience a discontinuity at

the reaction rim which influences the resulting products. There are those which experience a very consistent ASR type reaction within the agglomerate, seeming to leave the surrounding cement unaffected. There are also agglomerates which react with varying consistency to produce a low Ca/Si and relatively stable C-S-H type material. The cause of these distinctly different reactions is unknown; however, it does not appear to be strictly related to agglomerates size, location, or alkalinity of the cement. It is possible that an agglomerate with more surface area has a greater ability to react. Reaction at a greater rate allows for an increase in the exchange of calcium ions while the paste is still immature. This allows for a more evenly distributed gel with a composition closer to C-S-H than ASR [18], which was observed throughout the mixture, while the agglomerates induced local ASR [51]. Further study of the packing density and surface area of agglomerates may provide a distinction between the reactions observed.

There was an influential effect of alkalinity on the reactivity of the mixtures. When compared to conventional SCMs in low alkali cement, Glass 1 consumed less Ca(OH)_2 than SF at the same age. After 28 days, both showed a consumption of Ca(OH)_2 greater than 10% relative to the control mixture. Glass performed similarly to GGBFS in terms of Ca(OH)_2 consumption. In high alkali cement, SF was far more reactive than Glass 1. When compared to GGBFS, Glass 1 and Glass 2 in high alkali cement performed similarly, with consumption greater than 10% beyond 28 days for both mixtures, and no indication of ASR.

A comparison between hydration in low alkali cement and high alkali cement shows that there is generally more Ca(OH)_2 in the low alkali mixtures. Since the higher alkalinity increases the pH of the pore solution, decreasing the solubility of Ca, this result is expected [52]. Unlike the high alkali mixtures, the low alkali mixtures demonstrated an increase in Ca(OH)_2 at 150 days for all mixtures. Other researchers have postulated that increased Ca(OH)_2 levels observed in glass bearing blends may be a result of glass constituents being

incorporated into C-S-H in the place of Ca from the cement powder, resulting in excess Ca(OH)_2 in the pore solution [18].

There are two competing mechanisms which control the Ca(OH)_2 content in the paste: the hydration of cement powder, which produces Ca(OH)_2 , and the pozzolanic or ASR reactions, which consume Ca(OH)_2 . The difficulty lies in distinguishing which reaction is consuming the Ca(OH)_2 , and in following the reaction products for each reaction individually. If the rate of glass dissolution is greater than the production of either pozzolanic C-S-H or ASR gel, then the Ca(OH)_2 level may be increased due to substitution of sodium for calcium in the C-S-H [18]. This seems to be the case for the low alkali cement containing glass. For mixtures containing GGBFS, the additional Ca(OH)_2 may be the result of the hydraulic cementitious properties of the material [3]. In the case of the high alkali cement, pozzolanic or ASR reaction is taking place between 28 and 91 days, after which the Ca(OH)_2 levels stay relatively constant. At this point, the production of Ca(OH)_2 from hydrating cement has slowed significantly, as has any other reactions consuming Ca(OH)_2 , or else they are balanced. If low alkalinity reduces the rate of glass dissolution, it is possible that the opportunity for pozzolanic and ASR reactions to take place in the young hydrating cement may have already passed before the silica could dissolve to significant completion.

The low alkali cement was observed to have more aluminate hydrate phases present than the high alkali cement for similar mixtures at the same ages. These additional phases may have been favoured as a result of the greater availability of Ca(OH)_2 in the low alkali mixtures. The temperature at which certain peaks occurred was observed to shift over time, and the Ca(OH)_2 peak for high alkali cement occurred at a lower temperature than that of the low alkali mixtures. Shifts observed in the peak temperatures over time and for different mixtures may be indicative of the development of different phases over time. Additional testing would be required to confirm this result with statistical confidence.

4.4 Conclusions

Two conventional SCMs, SF and GGBFS, and two comparable particle sizes of waste glass, Glass 1 and Glass 2, were used as cement replacement materials in cements with high and low levels of alkalis in order to compare the performance of glass to traditional SCMs. The effects of the particle size, surface area, and alkalinity were observed. Mass loss of Ca(OH)_2 was used as a measure of the pozzolanic and ASR reactions taking place, and the presence of ASR was identified using optical and SEM methods. From the results of this testing program, the following conclusions are drawn:

1. When ground to a particle size comparable to SF, waste glass is less reactive and results in less pozzolanic reaction due to the difference in surface areas, where the SF has a surface area nearly ten times greater than that of the glass.
2. When ground to a particle size comparable to GGBFS, waste glass is equivalently reactive based on the consumption of Ca(OH)_2 as a measure of pozzolanic reaction since the surface area of the two materials is similar.
3. Use of low alkali cement results in calcium aluminate hydrate phases which are not present in the equivalent high alkali mixtures.
4. A well distributed glass ranging in particle sizes from 0.3-100 μm does not result in ASR gel formation up to 150 days under normal curing conditions.
5. Agglomerations of fine glass particles can initiate localized ASR. The composition of the reaction products can range from a low Ca/Si C-S-H, which does not tend to fluoresce, to a high alkali, low calcium material which demonstrated physical characteristics similar to ASR gel.
6. The composition and characteristics of reacted agglomerates is not strictly dependent on location or proximity to other agglomerates, alkalinity of the cement, or size of the agglomerate.

7. The composition of the reaction rim surrounding an agglomerate demonstrates a unique composition, and can influence the composition of both the reacted agglomerate and the surrounding paste.

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Reference List

- [1] Dubovoy VS, Gebler SH, Klieger P, Whiting DA. Effects of ground granulated blast-furnace slag on some properties of pastes, mortars, and concretes. In: Frohnsdorff G, editor. Blended Cements, ASTM STP 897. Philadelphia: American Society for Testing and Materials; 1986. pp. 29-47.
- [2] Hooton R D. Permeability and pore structure of cement pastes containing fly ash, slag, and silica fume. In: Frohnsdorff G, editor. Blended Cements, ASTM STP 897. Philadelphia: American Society for Testing and Materials; 1986. pp.128-143.
- [3] Malhotra VM, Mehta PK.. Pozzolanic and Cementitious Materials. In: Advance in Concrete Technology. New York: Gordon and Breach Publishers; 1996. ch. 1,4, pp. 5,11,39.
- [4] Detwiler RJ, Bhatti JI, Bhattacharja S. Supplementary Cementing Materials for Use in Blended Cements. Skokie, Illinois, U.S.A.: Research and Development Bulletin RD112T, Portland Cement Association; 1996.

- [5] Cook DJ. Natural pozzolans. In: Swamy, R.N, editor. Cement Replacement Materials, Vol. 3. London: Surrey University Press; 1986. pp. 1-39.
- [6] Rehan R, Nehdi M. Carbon dioxide emissions and climate change: policy implications for the cement industry. *Environ Sci Policy*. 2005;8:105-14.
- [7] World Business Council for Sustainable Development. The Cement Sustainability Initiative. In: Cement Sustainability Initiative. World Business Council for Sustainable Development. 2002. <http://www.wbcasd.org/DocRoot/11BetsIPgkEie83rTa0J/cement-action-plan.pdf> . Accessed 1 Mar 2010.
- [8] Meyer C, Baxter S, Jin W. Potential of Waste Glass for Concrete Masonry Blocks. In: Chong KP, editor. Proceedings of the Fourth Materials Engineering Conference. Washington:American Society of Civil Engineering; 1996. pp. 666-73.
- [9] Shao Y, Lefort T, Moras S, Rodriguez D. Studies on concrete containing ground waste glass. *Cem Conc Res*. 2000;30,1:91-100.
- [10] Shayan A, Xu A. Value-added utilization of waste glass in concrete. *Cem Concr Res*. 2004;34:81-9.
- [11] Laldji S, Tagnit-Hamou A. Glass frit for concrete structures: a new, alternative cementitious material. *Can J Civ Eng*. 2007;34:793-802.
- [12] Meyer C, Egosi N, Andela C. Concrete with waste glass as aggregate. In: Proceedings of the International Symposium Concrete Technology Unit of ASCE and University of Dundee. Dundee: 2001. pp. 179-87.
- [13] Polley C, Cramer SM, and de la Cruz RV. Potential for Using Waste Glass in Portland Cement Concrete. *J Mater Civ Eng*. 1998;10:210-19.
- [14] Day RL, Shi C. Influence of the fineness of pozzolan on the strength of lime natural-pozzolan cement pastes. *Cem Concr Res*. 1994;24,:1485-91.
- [15] Shi C, Day RL. Comparison of different methods for enhancing reactivity of pozzolans. *Cem Concr Res*. 2001;31:813-18.

- [16] Shi C, Wu Y, Riefler C, Wang H. Characteristics and pozzolanic reactivity of glass powders. *Cem and Concr Res.* 2005;35:987-93.
- Schwarz N, Neithalath N. Influence of a fine glass powder on cement hydration: Comparison to fly ash and modeling the degree of hydration. *Cem Concr Compos.* 2008;30:486-96.
- [17] Dyer TD, Dhir RK.. Chemical reactions of glass cullet used as cement component. *J Mater Civ Eng.* 2001;13:412-17.
- [18] Diamond S, Thaulow N. A study of expansion due to alkali-silika reaction as conditioned by the grain size of the reactive aggregate. *Cem Concr Res.* 1974;4:591-607.
- [19] Jin W, Meyer C, Baxter S. "Glascrete"-Concrete with glass aggregate. *ACI Materi. J.* 2000;97:208-13.
- [20] Pike RG, Hubbard D, Insley H. Mechanisms of alkali-aggregate reaction. *ACI J Proc.* 1955;52:13-34.
- [21] Tang M-S, Xu Z-Z, Han S-F. Alkali reactivity of glass aggregate. *Durab Build Mater.* 1987;4:377-85.
- [22] Struble, LJ, Diamond, S. Swelling properties of synthetic alkali silica gels. *J Am Ceram Soc.* 1981;64,11:652-5.
- [23] Jin W. Alkali-silica reaction in concrete with glass aggregate-A chemophysico-mechanical approach. PhD Thesis. New York:Columbia University; 1998.
- [24] Vessalas K, Thomas PS, Ray AS, Guerbois J-P, Joyce P, Haggman J. Pozzolanic reactivity of the supplementary cementitious material pitchstone fines by thermogravimetric analysis. *J Therm Anal Calorim.* 2009;97:71-6.
- [25] Kosmatka SH, Kerkhoff B, Panarese WC, MacLeod NF, McGrath RJ. Design and Control of Concrete Mixtures, 7th Ed. Ottawa: Cement Association of Ottawa; 2002.

- [27] Pane I, Hansen W. Investigation of blended cement hydration by isothermal calorimetry and thermal analysis. *Cem Concr Res.* 2005;35:1155-64.
- [28] Bhatti JI. A review of the application of thermal analysis to cement - admixture systems. *Thermochim Acta.* 1991;189:313-50.
- [29] Ramachandran VS. Thermal Analysis. In: Ramachandran VS, Beaudoin J J, editors. *Handbook of Analytical Techniques in Concrete Science and Technology.* New Jersey: Noyes Publications; 2001. pp. 127-73.
- [30] Wang KS, Lin K.L, Lee TY, Tzeng BY. The hydration characteristics when C_2S is present in MSWI fly ash slag. *Cem Concr Compos.* 2004;26: 323-30.
- [31] Taylor HFW. *Cement Chemistry.* Toronto: Academic Press; 1990.
- [32] El Elaoui B, Benkaddour M. Hydration of C_3A in the presence of $CaCO_3$. *J Therm Anal.* 1997;48:893-901.
- [33] Alarcon-Ruiz L, Platret G, Massieu E, Ehlacher A. The use of thermal analysis in assessing the effect of temperature on a cement paste. *Cem Concr Res.* 2005;35:609-13.
- [34] Marsh BK., Day RL, Bonner DG. Strength gain and calcium hydroxide depletion in hardened cement pastes containing fly ash. *Mag Concr Res.* 1986;38:23-9.
- [35] Chaipanich A, Nochaiya T. Thermal Analysis and microstructure of Portland cement-fly ash-silica fume pastes. *J Therm Anal Calorim.* 2010;99:487-93.
- [36] Ramachandran, V. S.; Paroli, Ralph M.; Beaudoin, James J.; Delgado, Ana H. *Handbook of Thermal Analysis of Construction Materials.* Norwich: William Andrew Publishing/Noyes; 2002.
- [37] Midgley AJ. The determination of calcium hydroxide in set portland cements. *Cem Concr Res.* 1979;9:77-82.
- [38] Natesaiyer K., Hover KC. In situ identification of ASR products in concrete. *Cem Concr Res.* 1988;18:455-63.

- [39] ASTM International, C856 - 04: Standard Practice for Petrographic Examination of Hardened Concrete. West Conshohocken: ASTM International; 2004.
- [40] Suwito, A, Jin, W, Xi, Y, Meyer, C. A mathematical model for the pessimum size effect of ASR in concrete. *Concr Sc Eng.* 2002;4:23-34.
- [41] Prezzi, M, Monteiro, PJM, Sposito, G. Alkali-silica reaction – part 2: the effect of chemical admixtures. *ACI Mater J.* 1998;95: 3-10.
- [42] Urhan, S. Alkali silica and pozzolanic reactions in concrete. Part 1: interpretation of published results and an hypothesis concerning the mechanism. *Cem Concr Res.* 1987;17:141-52.
- [43] Diamond, S. Chemistry and other characteristics of ASR gels. In: *Proceedings of the 11th International Conference on Alkali-Aggregate Reaction.* Quebec; 2000. pp.31-9.
- [44] Scrivener, KL, Monteiro, PJM. The alkali-silica reaction in a monolithic opal. *J Am Ceram Soc.* 1994; 77:2849-56.
- [45] Diamond, S, Sahu, S, Thaulow, N. Reaction products of densified silica fume agglomerates in concrete. *Cem Concr Res.* 2004;34:1625-32.
- [46] Dhir, R. K. Pulverized-fuel ash. In: Swamy, R N, editor. *Concrete Technology and Design Volume 3, Cement Replaceemnt Material.* Glasgow: Surrey University Press; 1986. pp. 197-255.
- [47] Mehta, P K. Influence of fly ash characteristics on the strength of portland-fly ash mixtures. *Cem Concr Res* 1985;15:669-74.
- [48] Pal, S C, Mukherjee, A, Pathak, S R. Investigation of hydraulic activity of ground granulated blast furnace slag in concrete. *Cem Concr Res.* 2003;33:1481-6.
- [49] Shi, C. Steel slag – its production, processing, characteristics, and cementitious properties. *J Mater Civ Eng.* 2004;16:230-6.

- [50] Lawrence, P, Cyr, M, Ringot, E. Mineral admixtures in mortars effect of type, amount, and fineness of fine constituents on compressive strength. Cem Concr Res. 2005;35:1092-1105.
- [51] Diamond S. Alkali silica reactions - some paradoxes. Cem Concr Compos. 1997;19:391-401.
- [52] Garci Jeunger MC, Jennings HM. Effects of high alkalinity on cement pastes 98-M28. ACI Mater J. 2001;98:251-5.

Table 4.1 Material composition and characteristics

%	LA	HA	SF	GGBFS	Glass 1	Glass 2
SiO ₂	20.41	19.65	94.90	35.85	71.59	72.06
TiO ₂	0.32	0.24	< 0.01	0.59	0.02	0.03
Al ₂ O ₃	5.54	5.56	< 0.01	10.52	1.78	1.81
Fe ₂ O ₃	2.33	2.61	0.05	0.67	0.13	0.07
CaO	65.06	64.32	0.40	36.74	10.73	10.81
MgO	3.33	2.54	0.66	12.74	0.18	0.21
MnO	0.07	0.04	0.04	0.57	< 0.01	< 0.01
SO ₃	2.63	3.20	0.11	3.60		
Na ₂ O	0.28	0.20	0.01	0.42	13.01	13.50
K ₂ O	0.24	0.79	0.63	0.47	0.40	0.40
LOI	2.19	3.46	3.01	1.23	2.32	1.00
Na ₂ O Eq.	0.44	0.72	0.42	0.73	13.27	13.76
C ₃ S	62.12	58.00				
C ₂ S	10.44	13.00				
C ₃ A	9.94	9.00				
C ₄ AF	6.84	8.00				

Table 4.2 Surface area

	LA	HA	SF	Glass 1	GGBFS	Glass 2
Surface Area/m ² g ⁻¹	1.99±0.10	2.57±0.13	20.67±1.03	2.32±0.12	1.82±0.09	1.59±0.08

Table 4.3 Mixture compositions

Mixture #	Composition	Mixture #	Composition
1	90% LA cement + 10% SF	6	90% HA cement + 10% SF
2	90% LA cement + 10% Glass 1	7	90% HA cement + 10% Glass 1
3	90% LA cement + 10% GGBFS	8	90% HA cement + 10% GGBFS
4	90% LA cement + 10% Glass 2	9	90% HA cement + 10% Glass 2
5	100% cement	10	100% cement

Table 4.4 Atomic % composition of agglomerates and surrounding material

		Ca	Si	Na + K	Ca/Si	(Na + K)/Ca
LA						
Range	Centre gel	3.1-21.1	7.5-22.2	0.8-6.4		
	Rim gel	6.1-20.4	9.3-30.5	1.5-4.6		
	Rim paste	5.6-9.2	2.1-13.9	1.9-2.5		
	Paste	0-27.6	1.9-19.1	0.9-8.0		
Average	Centre gel	9.2	15.3	3.1	0.6	0.3
	Rim gel	10.8	17.2	2.8	0.6	0.3
	Rim paste	7.4	8.5	2.2	0.9	0.3
	Paste	11.9	6.2	2.7	1.9	0.2
HA						
Range	Centre gel	0-15.3	2.1-22.8	1.5-19.6		
	Rim gel	4.1-15.6	1.8-26.8	1.0-9.6		
	Rim paste	4.6-15.0	1.7-10.3	0.7-7.3		
	Paste	6.8-35.7	1.6-10.7	0-4.5		
Average	Centre gel	7.7	12.5	5.4	0.6	0.7
	Rim gel	7.5	12.7	4.5	0.6	0.6
	Rim paste	10.6	6.3	3.0	1.7	0.3
	Paste	13.1	5.1	2.2	2.6	0.2

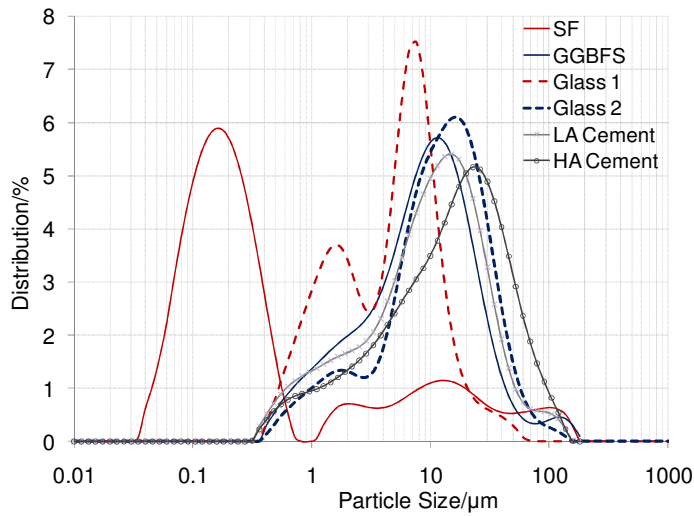


Figure 4.1 Particle size distribution of cementing materials

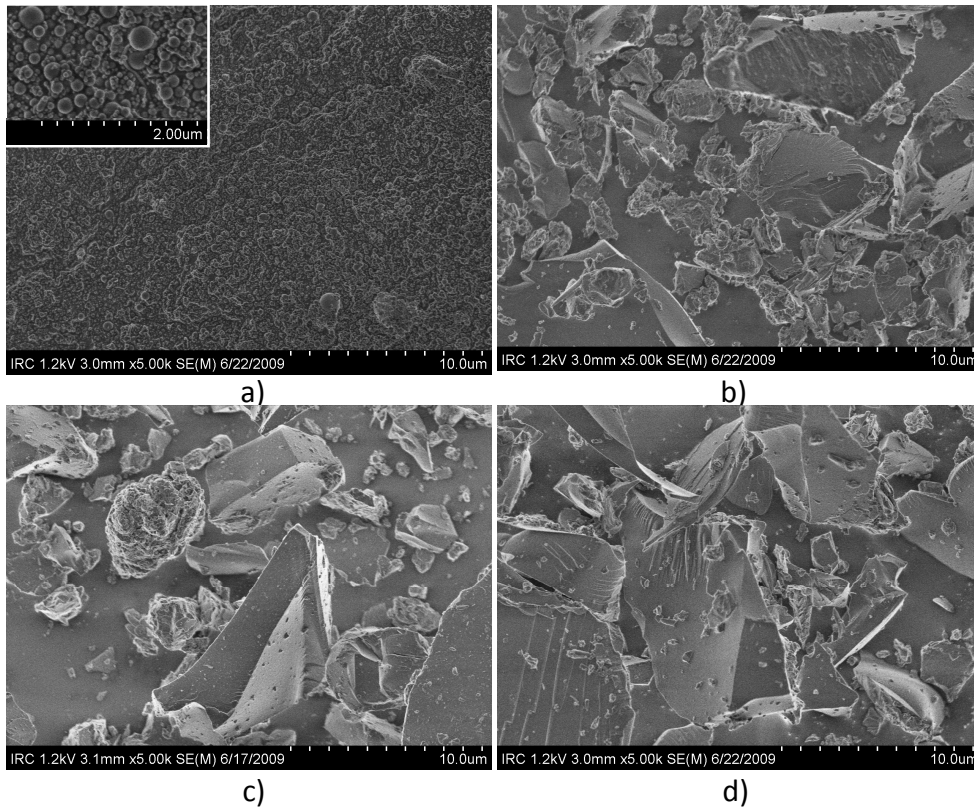


Figure 4.2 SEM images of **a** SF, *inset* at x5 higher magnification, **b** Glass 1, **c** GGBFS, **d** Glass 2

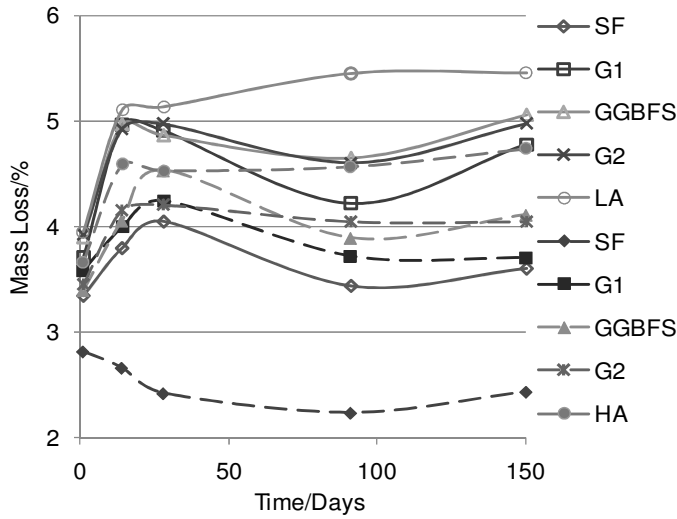


Figure 4.3 Amount of Ca(OH)_2 mass loss determined by thermogravimetric analysis at 3, 14, 28, 91, and 150 days hydration for paste samples made with low alkali cement (*solid line – LA*) and high alkali cement (*dashed line – HA*)

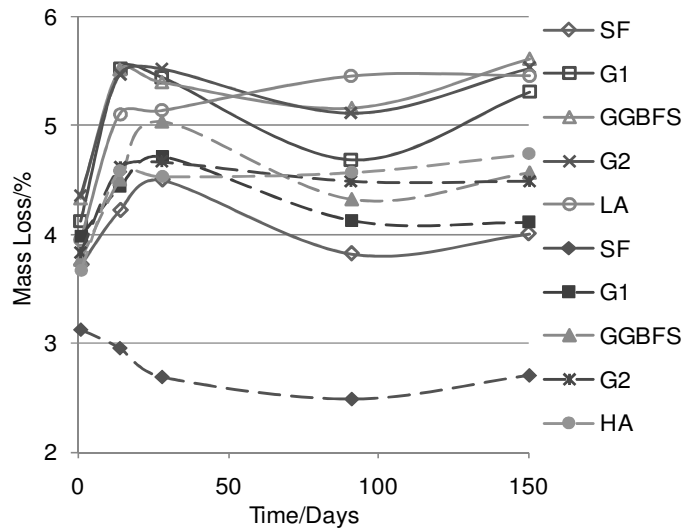


Figure 4.4 Change in Ca(OH)_2 content per unit weight anhydrous cement for paste samples made with low alkali cement (*solid line – LA*) and high alkali cement (*dashed line – HA*)

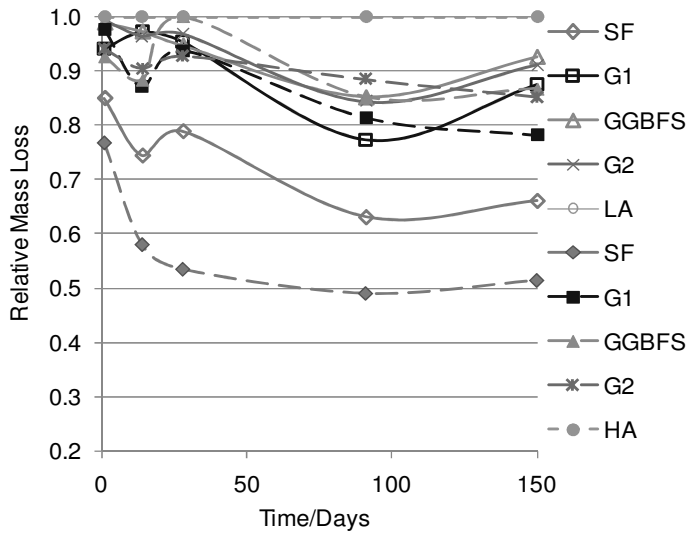


Figure 4.5 Ca(OH)_2 consumption relative to control mixture for paste samples made with low alkali cement (*solid line* – LA) and high alkali cement (*dashed line* – HA)

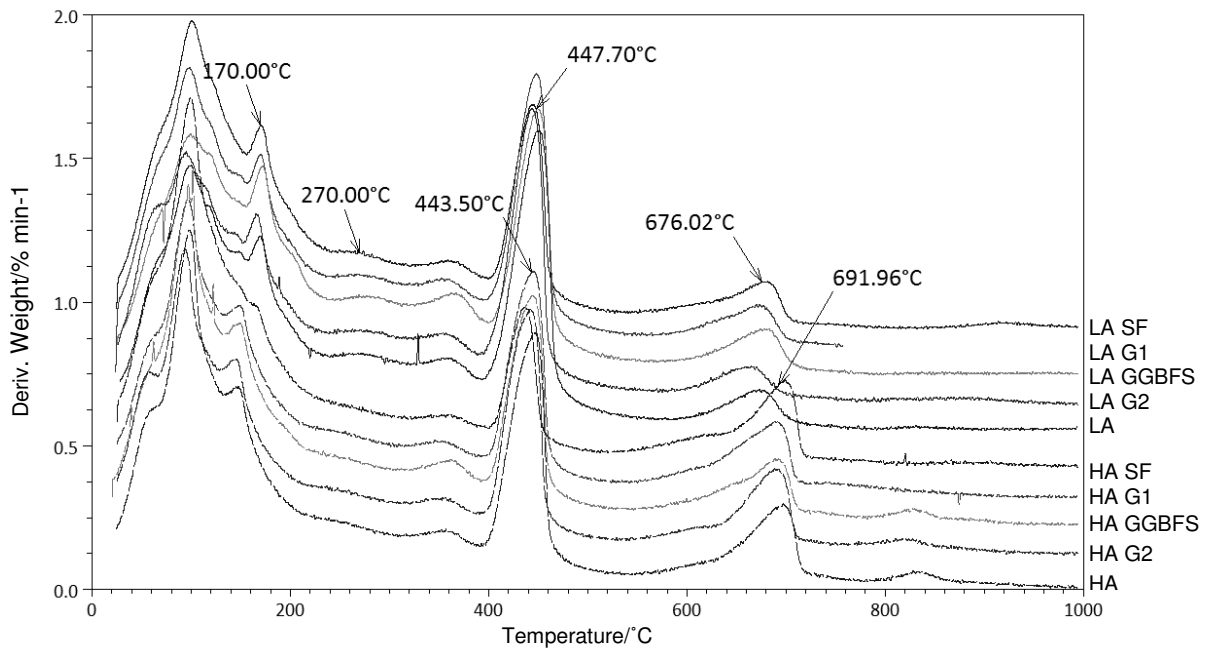


Figure 4.6 Differential thermal analysis of LA and HA mixtures at 28 days

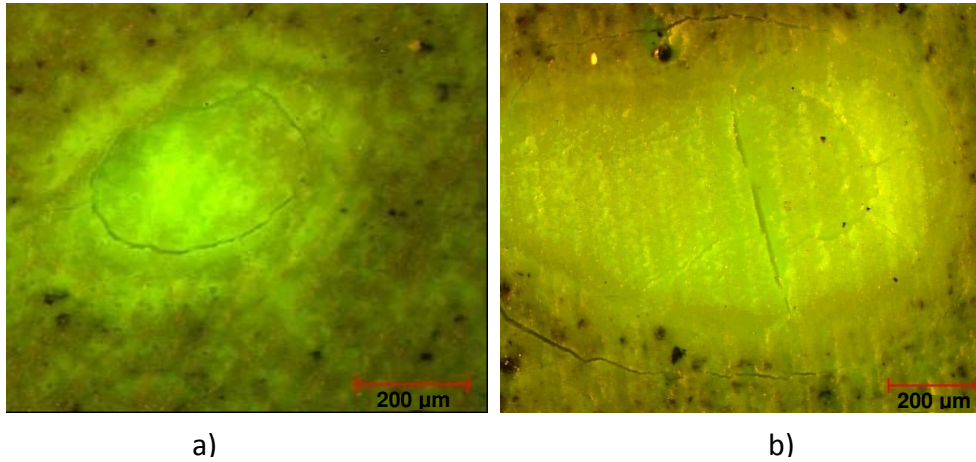


Figure 4.7 Optical images for **a)** mixture 2 (low alkali) and **b)** mixture 7 (high alkali) with glass agglomerate, reaction rim and fluorescing

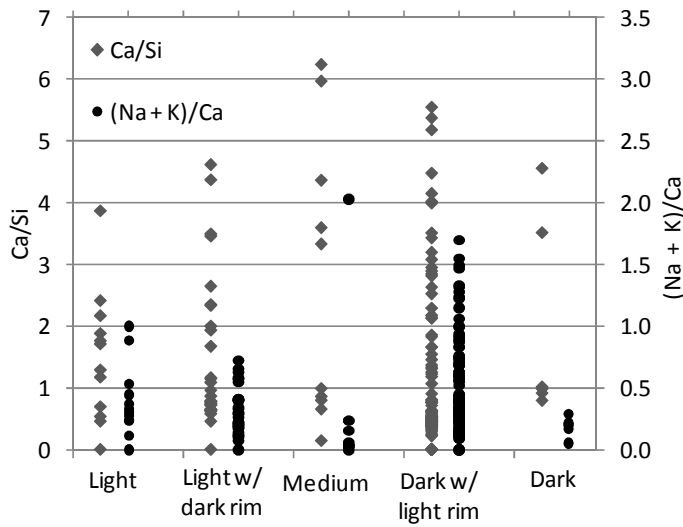


Figure 4.8 Composition versus colour of agglomerate in mixtures 2 and 7

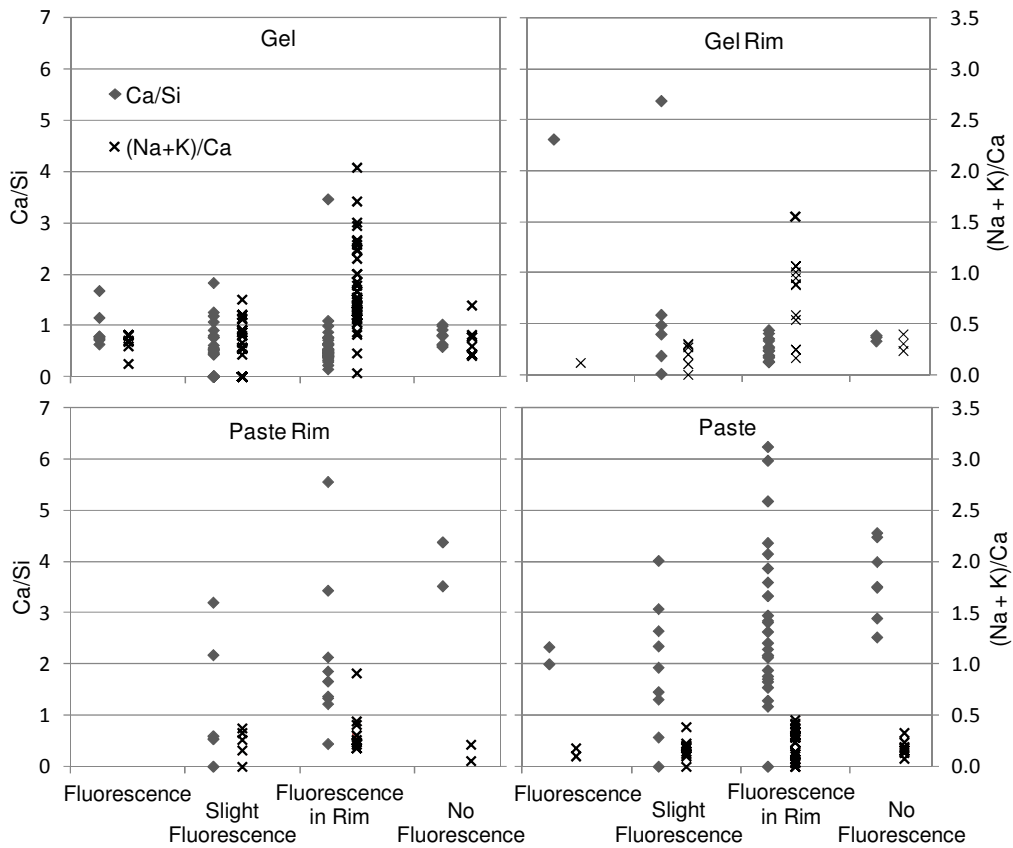


Figure 4.9 Composition versus fluorescence of the agglomerate of interest for different locations in and around agglomerates